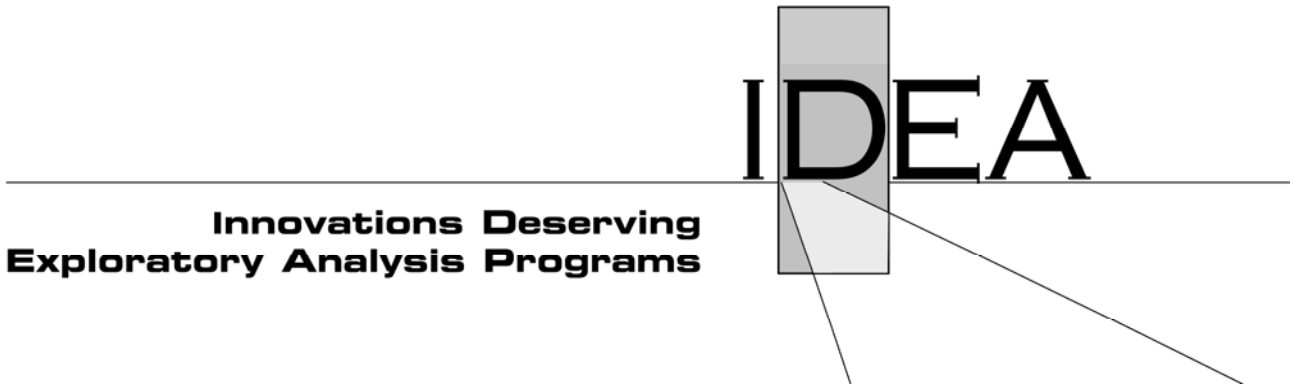

Highway IDEA Program

Evaluation of Novel Methods to Measure Water-to-Cement Ratio of Fresh Concrete

Final Report for Highway IDEA Project 105

Prepared by:
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September 2007

TRANSPORTATION RESEARCH BOARD
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Final Report

Evaluation of Novel Methods to Measure Water-to-Cement Ratio of Fresh Concrete

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PUBLISHED:

SEPTEMBER 2007

PREPARED FOR:

National Academy of Sciences

DISTRIBUTION:

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EXECUTIVE SUMMARY

This section represents an overview of the systematic approach used by the investigators to evaluate novel methods for determining the water-cement ratio (*W/C*) or water-to-cementitious-materials ratio (*W/CM*) of fresh concrete and how this approach led to the development of an improved method for measuring *W/C*. A graphical representation of the investigative approach is shown in Figure 1. Throughout this document, the nomenclature "*W/C*" will be used whenever the investigation utilized mixes with portland cement only, whereas "*W/CM*" will be used whenever supplementary cementitious materials (e.g. fly ash) were included in the investigation.

The investigators began by evaluating turbidity as a means for measuring *W/C* (via the Kansas Water/Cement Meter). This evaluation was based on prior research done by Kansas State University which resulted in a patented device (U.S. Patent No. 5,396,790) that was supposedly validated as being able to accurately quantify *W/C*. The investigators determined that the previous research on the Kansas device was erroneous apparently due to confounding of variables in the experimental design. Further testing and analysis by the investigators showed that the device is very sensitive to cement variations but very *insensitive* to water variations and thus unable to reliably measure *W/C*. However, the investigators hypothesized that turbidity could still be a viable means to measure *W/C* if the sample could be reduced to a binary mix (i.e. water and cement only): by calculating the cement content using turbidity (and specimen volume or mass), the water content would be known, along with *W/C*. This concept is discussed further in Section 1.

Several other methods for determining *W/C* were also evaluated:

- *Gamma Radiation Absorption* (*GRA*) (Section 2.1) – A gamma ray densitometer was evaluated on water-cement mixtures having different *W/CMs* as well as individual mix constituents. The data demonstrated that *GRA* could be used to measure the relative densities of mixtures at low energy levels (i.e. below 100 keV). However, the method was unable to distinguish differences in mineralogy between mix constituents. As such, *GRA* could be used to measure the composite density of a given mix, but would not provide needed information regarding the relative proportions of any of the mix constituents.
- *Fluorescence & Standard Addition* (Section 2.2) – The investigators attempted to determine the water levels of a concrete mix via fluorometric measurements with a fluorescent dye. Rhodamine was added as a dye to specimens of fresh concrete and emission spectra were captured at a wavelength of 560nm. Incremental dilutions were tested on each specimen, and the emission spectra were again captured. This method was unable to reliably measure the percentages of each specimen's constituent materials apparently due to the dye being adsorbed to the solids in the specimen. As a result, the method may have potential use in determining the specific surface of concrete's constituent materials, but not currently suitable as a means to measure water content (or, consequently, *W/C*) in a concrete mix.
- *Specific Gravity* (Section 2.3) – The investigators devised a measurement procedure wherein volumetric and specific gravity relationships could be used to mathematically determine the water-to-cementitious-materials ratio (*W/CM*). By calculating the density

of a mortar specimen along with the volumetric ratios of cementitious-materials-to-solids (*CM/S*) and fly-ash-to-cementitious-materials (*F/CM*), the water-to-solids ratio (*W/S*) and solids-to-cementitious-materials ratio (*S/CM*) could be quantified, thus yielding *W/CM* (as the quotient of *W/S* and *S/CM*). Three mini-procedures were developed to calculate each parameter, and the results showed that this method is capable of yielding good precision as a means for measuring W/CM of mortar specimens. An expanded test was later conducted to evaluate the method's precision with concrete specimens (see Section 3).

- *Microwave-Oven-Drying* (Section 2.4) – The conventional *Microwave-Oven-Drying* method was researched and evaluated. The error with this method was identified as being primarily due to the inability to accurately account for moisture in the coarse aggregate. Improvements to the method were implemented and evaluated. The improved method and its evaluation are described in Section 5.

Systematic Evaluation of Methods for Determining *W/CM*

Figure 1 shows the progression of methods evaluated by the investigators, the pitfalls that surfaced with each method, and the innovations employed by the investigators to overcome difficulties, apply lessons learned, and make meaningful progress throughout the investigation.

As can be seen by Figure 1, both the *Gamma Radiation Absorption* (*GRA*) and the *Fluorescence and Standard Addition* (*FSA*) methods resulted in difficulties that could not be overcome within the scope of the current investigation. With *GRA*, the composite density for a given concrete mixture was measureable; however, *GRA* was unable to directly measure the relative proportions of individual mix constituents. With *FSA*, the investigators observed that the fluorescent dye seemed to adsorb to the solid particles in the mix rather than remaining entirely suspended in the free water. This occurrence limits the ability of the method to be used for measuring *W/C* or *W/CM*, but shows promise as a possible method to measure the overall surface area or specific surface of the solid particles in the mix, which could be beneficial as a quality control tool.

As previously mentioned, the *Turbidity* method as implemented by the Kansas device was found to be very sensitive to changes in cement content but very *insensitive* to changes in water content, and thus not able to measure *W/C*. As such, *Turbidity*, at least as used in accordance with the Kansas device, was deemed inadequate as a means to measure *W/C* or *W/CM*.

Concurrent with their evaluation of the *Turbidity* method, the investigators evaluated *Specific Gravity* as a means for measuring *W/CM*. This evaluation yielded three promising results:

- Water-to-solids ratio (*W/S*) could be successfully measured via specific gravity measurements and a few simple calculations.
- Cementitious-materials-to-solids ratio (*CM/S*) could be successfully measured using a sedimentary settlement column.
- Water-to-cementitious-materials ratio (*W/CM*) could be determined as the quotient of *W/S* and *S/CM*.

In addition, a secondary evaluation was performed and demonstrated that red-green-blue (RGB) imaging could be used to determine the amount of fly ash present in a mortar mixture containing both portland cement and fly ash.

The primary drawback to the investigators' initial evaluation of the *Specific Gravity* method was the fact that the initial investigation utilized mortar mixes (sand, cement, fly ash, water) rather than genuine concrete mixes (i.e. with coarse aggregate). As such, the investigators recognized that the next step to validating the *Specific Gravity* method needed to involve "normal" concrete mixes incorporating all the primary constituent materials found in standard portland cement concrete. As the investigators set out to do this, they also decided to incorporate some lessons learned from the *Turbidity* evaluation.

While analyzing the problems inherent with the Kansas *Turbidity* device, the investigators recognized that *Turbidity* could be successfully used to measure and/or assist with measuring *W/C* under either of two circumstances:

- Extract the paste-only from the concrete specimen, then measure either the water content or the cement content of the paste (using either *Turbidity* or *Specific Gravity*), or
- Use *Turbidity* to measure cement content and employ a separate method (e.g. *Specific Gravity*) to determine the water content.

As such, the investigators decided to pursue both the above options and, in so doing, to integrate *Specific Gravity* and *Turbidity* during the next stage of the investigation. In the first instance (paste extraction), both *Specific Gravity* and *Turbidity* were used to independently measure *W/C*. With the second option, cement content was measured via *Turbidity* and water content via *Specific Gravity*.

The *Paste-Extraction* method (discussed in Section 4) employed two screening processes, one for removing the coarse aggregate and a second for removing fine aggregate. The investigators were successful in removing the coarse aggregate from all mixes and were able to effectively screen the fine aggregate for relatively wet mixes (i.e. *W/C* above 0.45). However, with relatively dry mixes (*W/C* below 0.45), the investigators were unable to extract enough paste to yield adequate precision.

Significant Innovation Resulting from the Research

After numerous successful trials with screening the coarse aggregate from various concrete mixes the investigators pursued a direction not originally intended. Realizing that a major difficulty with the conventional *Microwave-Oven-Drying* method was the inability to adequately account for variations of moisture within the coarse aggregate, the investigators decided to evaluate the *Microwave-Oven-Drying* method with the addition of a coarse-aggregate screening process. Initial results showed that the revised method was very accurate in determining water content for both wet and dry mixes. However, even though the water content of the screened specimen could be measured and then used to calculate the water-to-solids ratio (*W/S*), it did not directly provide the desired measurement, *W/CM*.

The investigators further recognized that *W/CM could* be quantified if the mass of fine aggregate (i.e. particles between 75 μm and 9.5 mm) in the screened specimen could be adequately measured. In other words, if the cementitious-to-solids ratio (*CM/S*) of the screened specimen could be determined, the *W/CM* could be easily calculated as the quotient of *W/S* to *CM/S*.

In order to obtain *CM/S*, a 55-micron filter bag was successfully utilized to segregate the fine aggregate from the screened specimen *after the specimen had been completely dried in the microwave oven*. The resulting process enabled the investigators to adequately account for the fine aggregate and thus precisely measure *CM/S*. The results showed that this method has good precision for all levels of *W/CM*. The method was simple to perform and took about 20 minutes per test. In addition, the method has strong potential to be automated, which should provide even better precision. This method is discussed in more detail in Section 5.

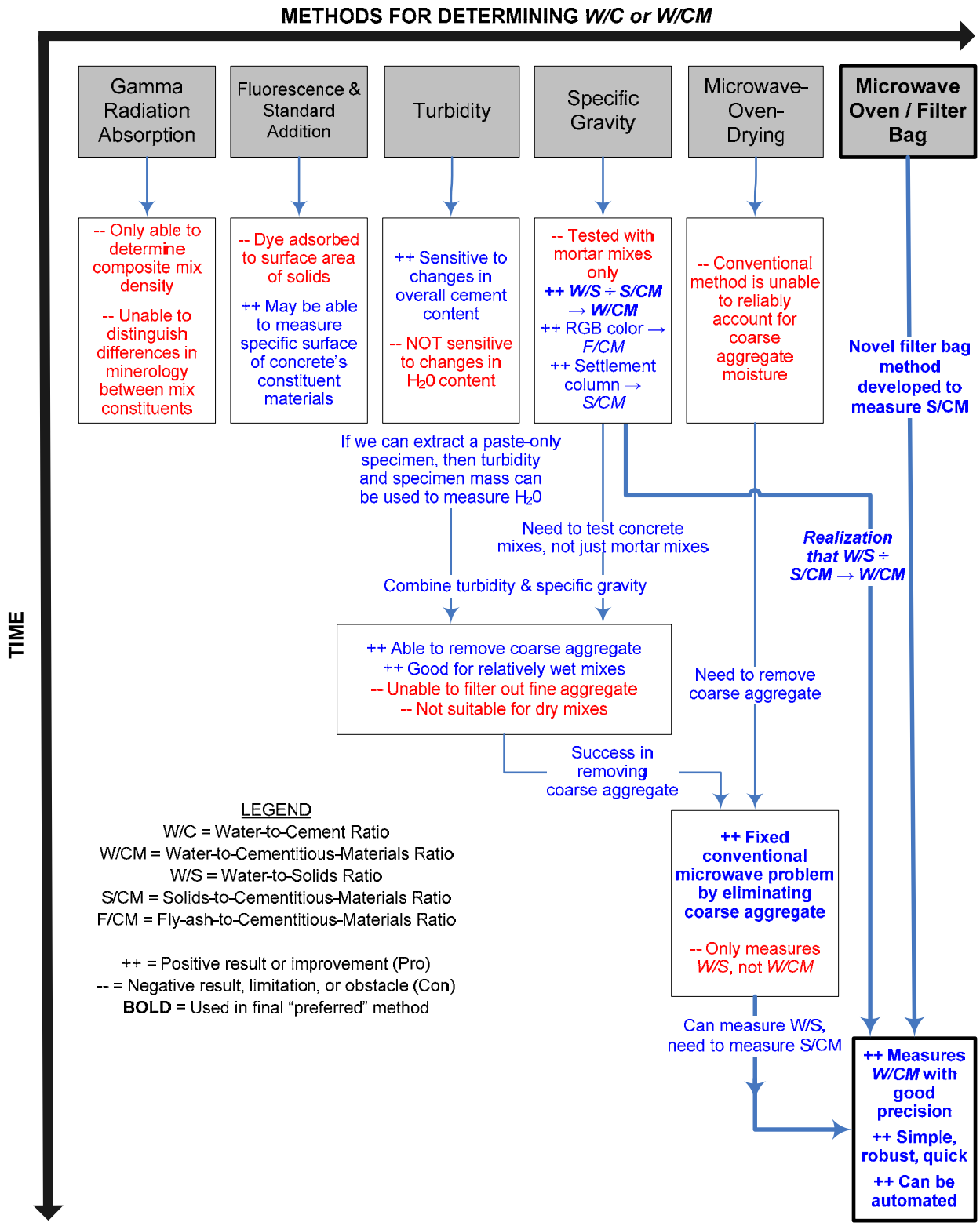

Figure 1: Investigation of Methods to Quantitatively Determine Water-to-Cement Ratio

BACKGROUND – THE EXPERIMENTAL APPROACH

Any experimentation performed using mixtures requires special consideration. This is due to the fact that, with mixtures, the experimenters can never change only one parameter at a time. Whereas the sum of the components for any mixture must always total 100%, adjusting one of the components necessitates changing at least one other component. Failure to properly consider this nuance can easily lead to confounding variables and erroneous conclusions.

The solution to this potential problem involves recognizing that there are several ways that the water-to-cement ratio (*W/C*) of any given "reference" mix can be altered. The first, and most obvious, is simply the addition of more water to the mix. This is analogous to what commonly occurs at the job site, where additional water is added to a transit mix prior to placement. The net effect of this is to proportionately decrease the relative percentages of ALL the other components in the mix. Figure 4 and Figure 5 demonstrate this. However, whereas this method changes ALL the components of the mixture, measurement sensitivity to ANY of the components can be easily mistaken as sensitivity to the change in water content. This can be seen in Figure 5 wherein all the solid constituent materials have a negative slope, meaning that their respective proportions are all decreasing with increasing *W/C*. This is apparently what led previous researchers to erroneously conclude that the Kansas Water/Cement Meter (see Section 1.3) could effectively measure *W/C*.

A second, quite common way for the water content (and thus *W/C*) to change for a given concrete mix is through changes in the amount of moisture above saturated surface dry (SSD) in the fine aggregates (i.e. sand). Such deviations from the designed water content occur because concrete aggregates are typically batched by weight; and, the weight of the excess water (i.e. above SSD) is *assumed* but not accurately or precisely *known*. As such, if the fine aggregate source contains significantly more water than is assumed, the net effect is more water and less fine aggregate in the final concrete mixture. Figure 6 and Figure 7 demonstrate this effect. Unlike Figure 5, Figure 7 shows that only two constituent materials are changing proportions – the fine aggregate and the water. Under this scenario, any measurement that is sensitive to changes in fine aggregate *and/or* water will be affected.

Similar to the fine aggregate moisture scenario, a third way for the water content to change is due to changes in the amount of moisture above SSD in the coarse aggregates. This will result in more water and less coarse aggregate as shown in Figure 8 and Figure 9. In this instance, Figure 9 shows that only the coarse aggregate and the water change with *W/C*. Under this scenario, any measurement that is sensitive to changes in coarse aggregate *and/or* water will be affected.

A fourth possible, though extremely uncommon, way for the *W/C* to increase would be through an increase in water content coupled with a corresponding decrease in the cement content. Figure 2 and Figure 3 demonstrate this for a paste-only example. Under this scenario, any measurement that is sensitive to changes in cement *and/or* water will be affected. This is the case with the Kansas device. Its high sensitivity to cement content shows up both under this scenario and the first scenario (where the relative proportions of all the mix constituents are changing). In other words, any validation of the Kansas device that relies solely upon this option

or the first option would erroneously conclude that the device is sensitive to changes in *W/C* when, in reality, it is only sensitive to changes in cement content.

In order to remove any confounding measurement sensitivities to proportion changes to other constituent materials, the investigators implemented each of the four aforementioned methods as a part of the experimental program.

	Low w/c w/c = 0.33			Medium w/c w/c = 0.50			High w/c w/c = 0.67		
	Units		% of Whole	Units		% of Whole	Units		% of Whole
Water	2	Water	25.0%	3	Water	33.3%	4	Water	40.0%
Cement	6	Cement	75.0%	6	Cement	66.7%	6	Cement	60.0%
	8	TOTAL	100%	9	TOTAL	100%	10	TOTAL	100%

Figure 2 – Effect of Additional Water to Relative Proportions of Other Constituents (Paste Only)

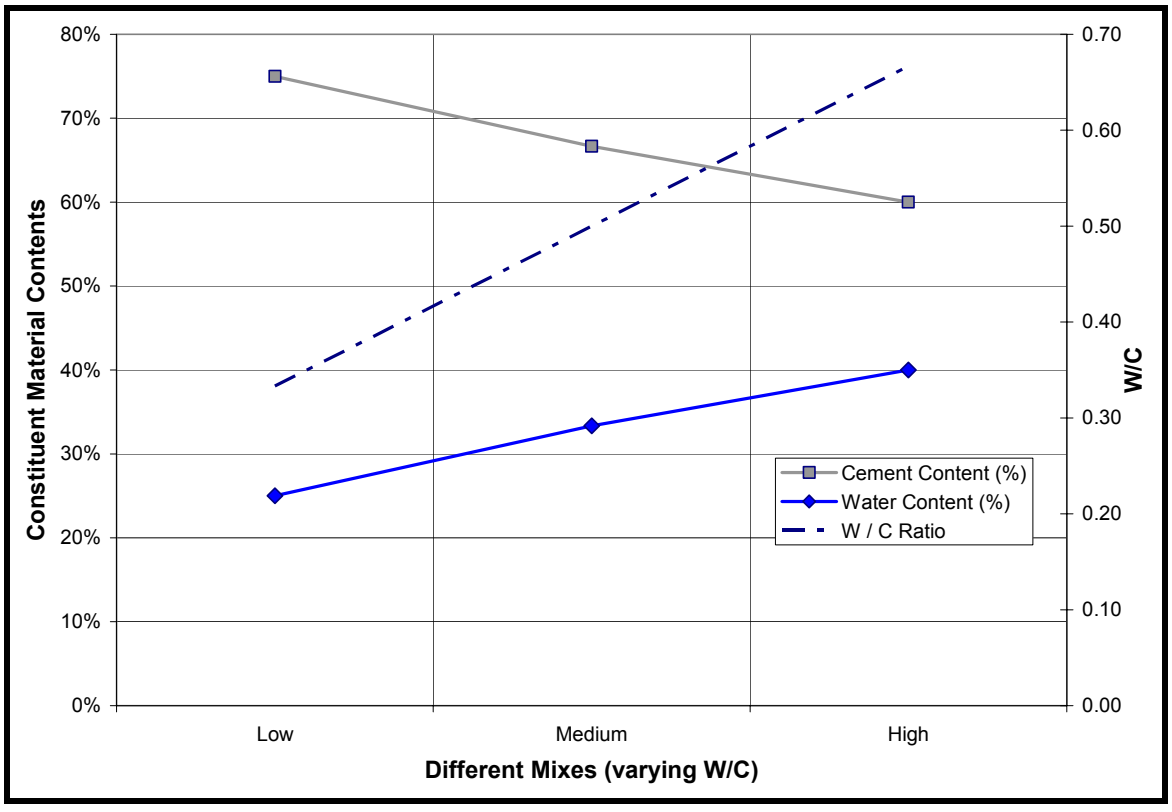

Figure 3 – Chart showing Effect of Additional Water to Relative Proportions of Other Constituents (Paste Only)

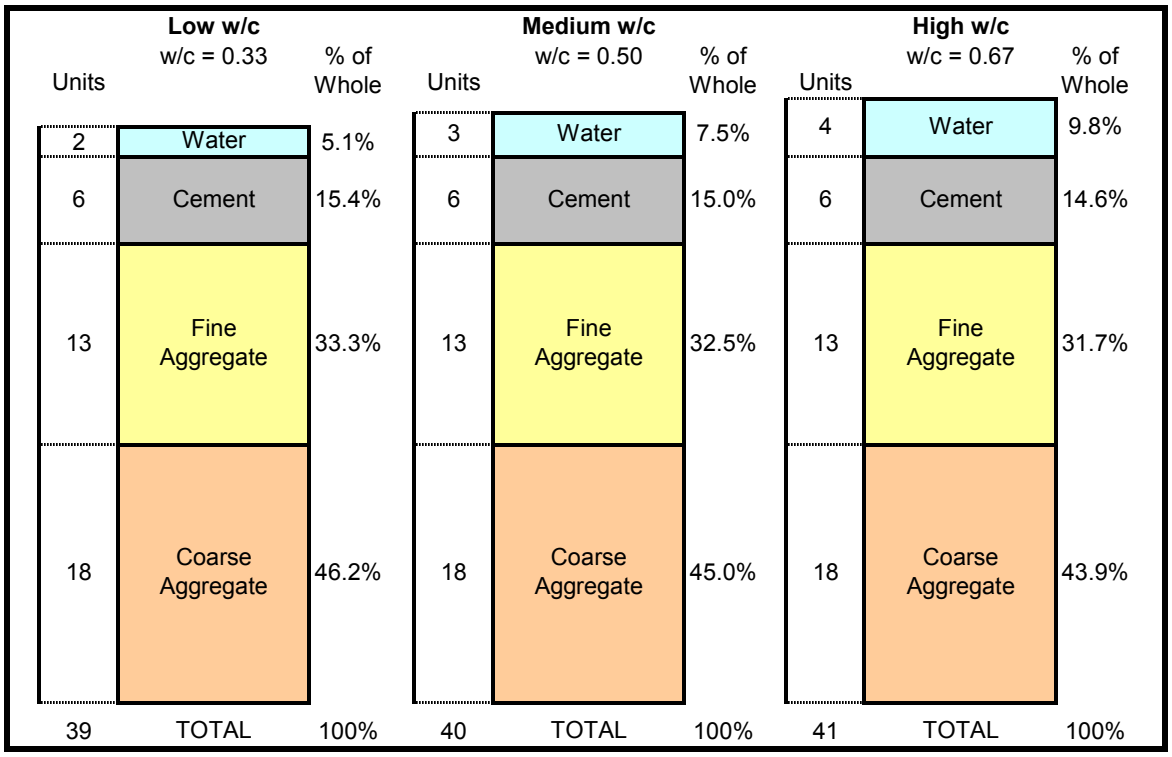

Figure 4 – Effect of Additional Water to Relative Proportions of Other Constituents

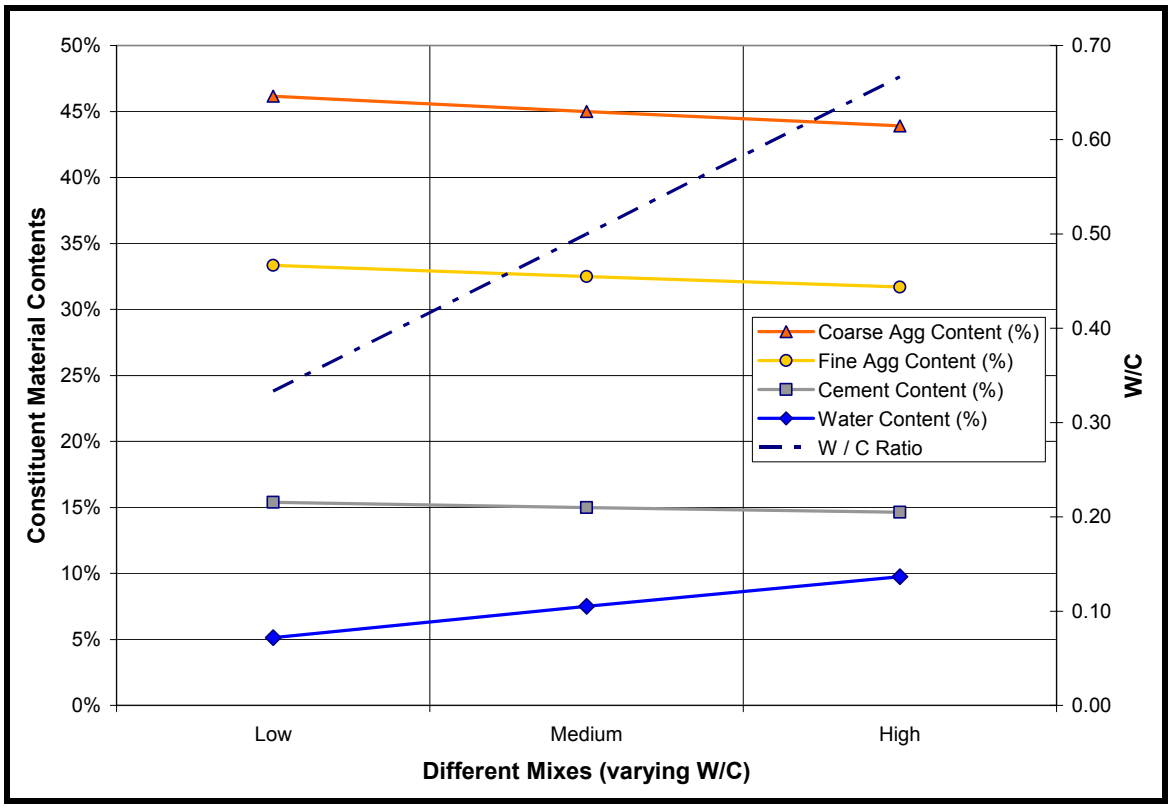

Figure 5 – Chart showing Effect of Additional Water to Relative Proportions of Other Constituents

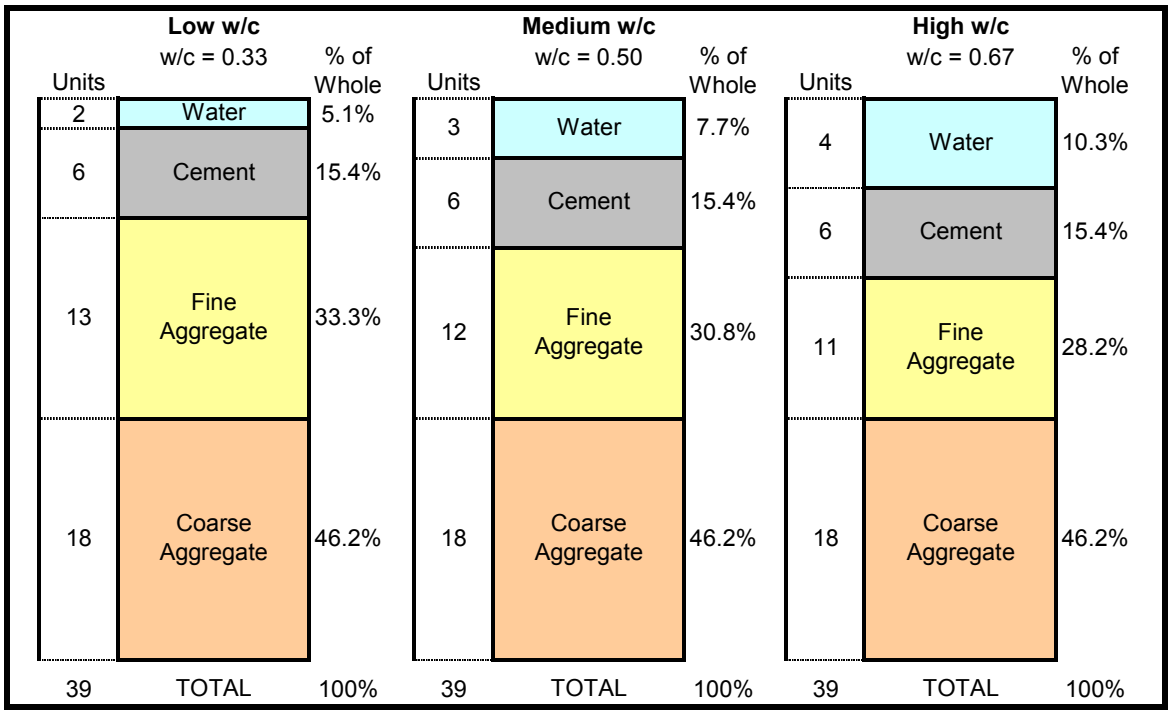

Figure 6 – Effect of Additional Water due to Changes in Fine Aggregate Moisture

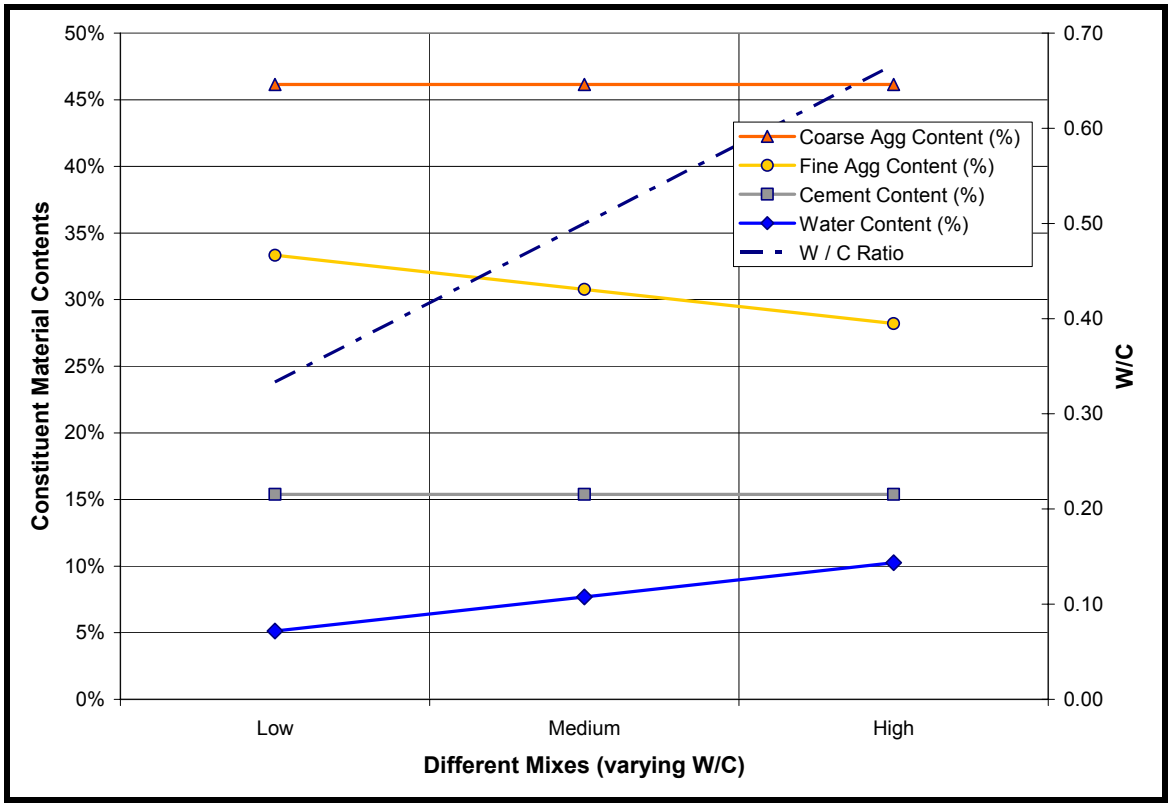

Figure 7 – Chart showing Effect of Additional Water due to Changes in Fine Aggregate Moisture

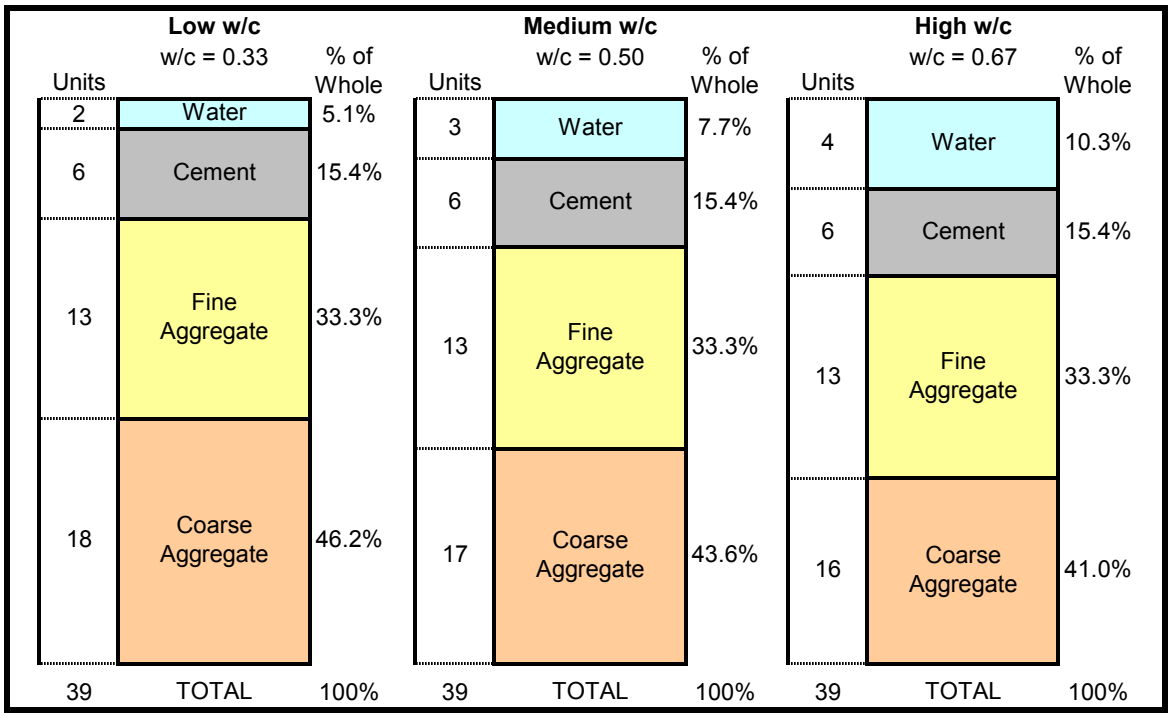

Figure 8 – Effect of Additional Water due to Changes in Coarse Aggregate Moisture

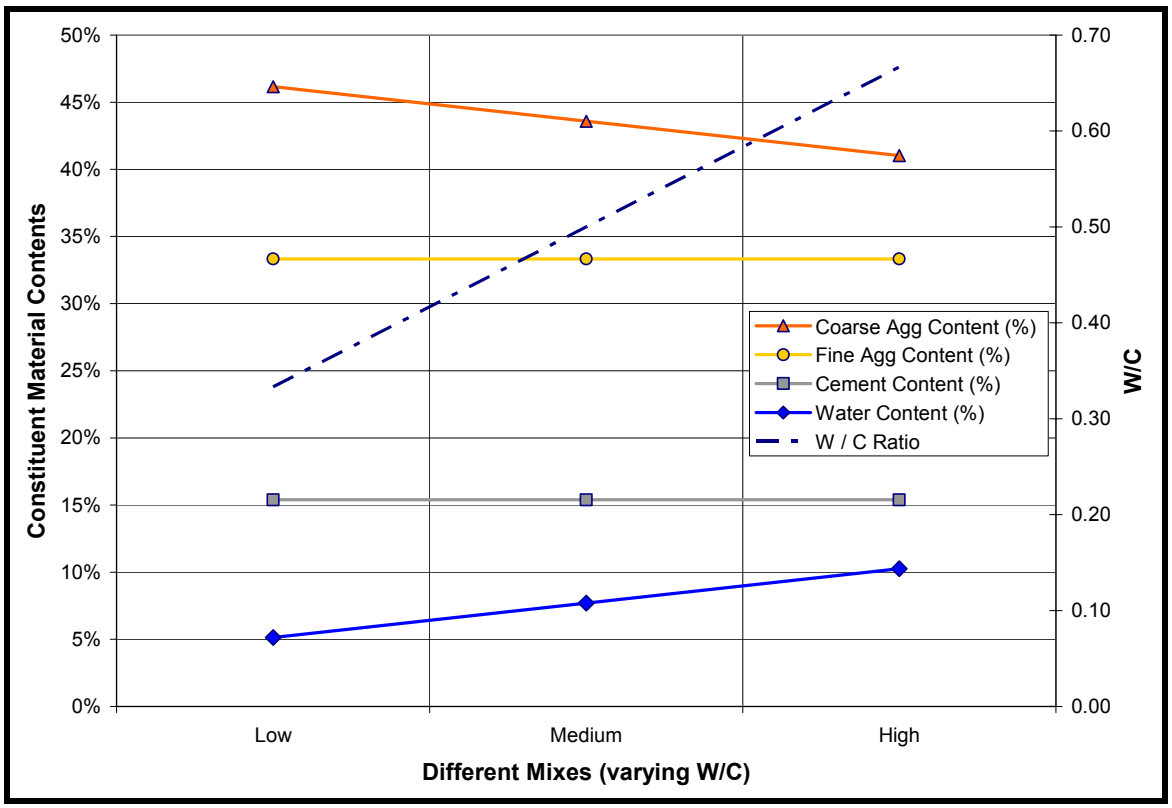

Figure 9 – Chart showing Effect of Additional Water due to Changes in Coarse Aggregate Moisture

1. EVALUATING TURBIDITY (VIA THE KANSAS WATER/CEMENT METER)

The investigators began by evaluating the Kansas Water/Cement Meter since it had been reported by Kansas State University researchers to be able to "measure the water-cement ratio of fresh concrete with an accuracy of ±0.01 on the water-cement ratio scale for a single test at a 90% confidence interval" (Hossain et al 1996). With this in mind, the Kansas device was acquired and tested using a mortar mix (i.e. cement, water, and sand only), and the following observations were made.

1.1 General Observations

The most notable observation made relative to the Kansas device involves the sensitivity of the device to the concrete constituent materials. Sensitivity of the device to concrete constituent materials is shown in Figure 10 and can be summarized as follows:

- Very sensitive to cement content (up to 0.25 lbs. total cement).
- Relatively *insensitive* to sand content.
- *Very insensitive* to water content.

Due to the insensitivity to water content, the device appears to be a good indicator of the *mass of cement* in the mixture, but NOT a good indicator of the *mass of water* or the *water/cement ratio*. As such, the investigators do not recommend any further evaluation, validation, refinement, or development of the Kansas device.

1.2 Operational Problems with the Device

The following operational problems surfaced during the evaluation of the Kansas device:

- **Sensor fogging** – The internal glass tube (through which the dilute cement slurry flows and through which the turbidity measurements are obtained) was very susceptible to fogging due to cement particles adhering to the interior surfaces of the tube.
- **Sensor over-range condition** – The turbidity ranges resulting from the recommended specimen sizes greatly exceeds the measurable values associated with the single-beam turbidimeter employed by the Kansas device. The sample sizes (1 pound of concrete) and dilution rates (20 pounds of water) recommended by the KSU research reports result in actual turbidity values one or two orders of magnitude higher than the device's measurable upper range (1,000 NTU). In addition, the device has no warning to identify that an over-range condition has occurred. As soon as the range of the sensor is exceeded (which occurs at less than 0.05 pounds of total cement), a quenching of the sensor begins, and the reported NTU values begin to fall with additional cement. This can be seen visually by the concave shape of the cement-sensitivity curve shown in Figure 10.
- **Sensor destroyed due to gasket failure** – During validation testing, the turbidimeter sensor was destroyed when an O-ring gasket failed, allowing the circulating water to flood the sensor's electronics. The turbidimeter manufacturer was contacted and the sensor was replaced.

1.3 Sensitivity of the Device to Water, Sand, and Cement

As stated above, the Kansas device did not exhibit the expected sensitivity to water/cement ratio. Figure 10 shows the relative sensitivity of the device to the primary constituent materials found in portland cement concrete. Two issues arise from the analysis of this data. The first and foremost issue deals with the fact that the device was insensitive to changes in water/cement ratio (and only to overall cement content) even though the research reports presented by Kansas State University (KSU) show otherwise. The second issue deals with the concave nature of the cement sensitivity curve. Each of these issues will be discussed below.

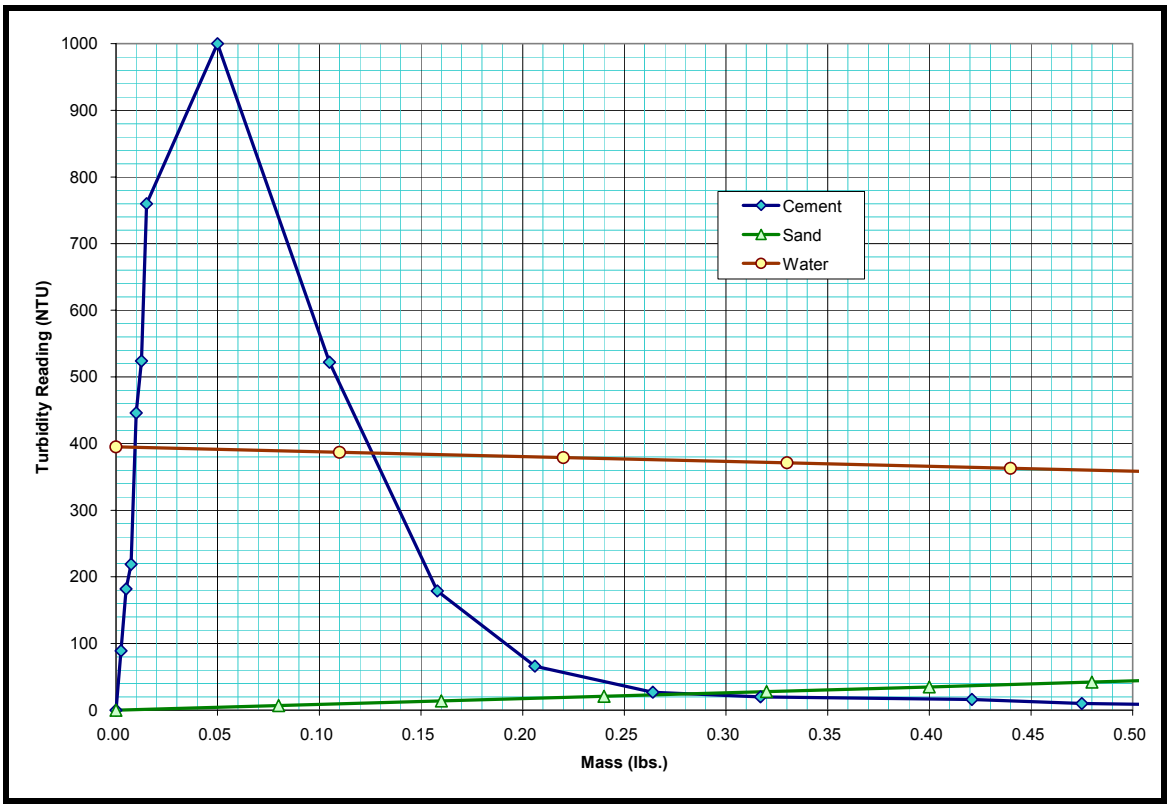

Figure 10 – Sensitivity of Kansas Water/Cement Ratio Meter to Concrete Constituent Materials

1.3.1 Sensitivity to Cement / Insensitivity to Water Content

The investigators were initially puzzled by the discrepancy between the results obtained during the current study and those published by KSU. However, upon closer examination, the investigators were able to determine the most likely reason for the discrepancy. Apparently, the KSU researchers confounded cement content with water/cement ratio during their validation experiments. In other words, every time the water/cement ratio was increased, the cement content was decreased. As such, the experiments were unable to distinguish between changes to water/cement ratio and changes to cement content. This error would have occurred if the aggregate proportion from mix to mix was held constant. With a binary mix (a mixture having only two components), it is impossible to isolate the effects of one component from the other (or from the ratio of the two). This is because *increasing* the proportion of one component requires that the relative amount of the other component be proportionately *decreased*. This problem also

occurs whenever a ternary mix is used but one of the mixture components is held constant (such as an aggregate/cement/water mix with the aggregate proportion held constant).

Apparently the KSU researchers held the aggregate content constant while adjusting only the water and cement proportions from mix to mix. Such a procedure would confound (or alias) the effects of water/cement ratio with cement content. To truly ascertain the effects of the individual components on the measured response, a mixture design experiment must independently vary at least three of the mixture components.

2. PRELIMINARY EVALUATION OF OTHER *W/C* MEASUREMENT METHODS

The investigators decided to research other methods (besides turbidity) for quantifying *W/C*. Four different methods were investigated in this preliminary evaluation, and three of those methods were evaluated via specimen testing.

2.1 Preliminary Evaluation: Gamma Radiation Absorption (GRA)

Another method investigated in this preliminary evaluation utilized a combination of several low-radiation sources on a cement paste mixture that would attempt to determine the specimen's composition and density via absorption analysis.

2.1.1 Fundamentals of Gamma Ray Densitometry

Gamma radiation is an electromagnetic radiation similar to X-rays. While X-rays are usually generated in X-ray tubes, gamma radiation is a by-product of the natural decay of certain radionuclides. Energies range from approximately 10 keV to 10 MeV. Gamma radiation of a sufficiently high energy can penetrate even metallic materials that are impermeable to X-rays.

The principle of gamma ray densitometry measurement is based on the absorption of gamma radiation in the tested material. The term 'absorption' in this context is used for any physical interaction between the radiation and the material such that a reduction in the intensity of the incident radiation penetrating the sample is observed.

2.1.1.1 Absorption of gamma radiation

Photons of gamma radiation can interact with the electrons of the tested material. Two different interaction processes are observed – the photoelectric effect and Compton scattering. Depending upon the energy of the radiation and the ordinal number of the tested material in the periodic table, either one of the two processes may predominate. The photoelectric effect is the interaction of a gamma photon with an electron in the inner shell of an atom. The gamma photon is completely absorbed and the electron uses the additional energy to leave its atom as a free (photo) electron. The Compton effect is the scattering of a gamma photon by an inner shell electron whereby only part of the photon's energy is transferred to the electron. The irradiated sample itself is not permanently affected by either of these interactions. In particular, it does not become radioactive.

The capability of a material to absorb gamma radiation is characterized by its absorption coefficient. All absorption processes contribute to the absorption coefficient. The photoelectric effect generally predominates at lower radiation energies, whereas the Compton effect is more predominant at higher radiation energies (i.e. more than 100 keV).

The absorption depends on both the composition (i.e. mineralogy) and the density of the material. The higher the density, the more electrons are available within a given volume to interact with the radiation and thus more radiation is absorbed. Hence, the material density can be determined from the intensities of the original and the attenuated gamma radiation.

2.1.1.2 Densitometer design

The basic design of a gamma ray densitometer is shown schematically in Figure 11. The 'heart' of the instrument is the radioactive source providing the gamma radiation. The source is mounted inside a shielding container. Radiation emerges from the container and passes through the test piece, then on to the detector.

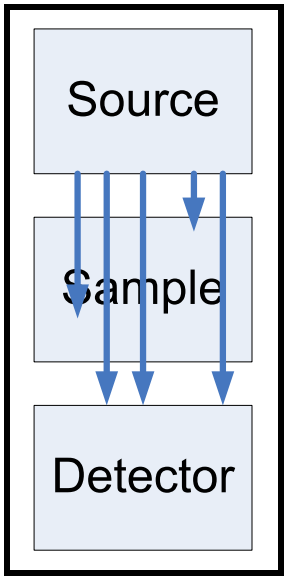

Figure 11 – Schematic showing the principal components of a gamma ray densitometer

In addition to the intensity of the radiation, the thickness of the test piece and the absorption coefficient of the material are parameters needed to calculate density.

2.1.1.3 Radiation source

Several radionuclides are available as radiation sources. The criteria for the selection of the radiation source are radiation energy, long service life, and availability. The investigators used a combination of several sources at once to get a broad spectral range of radiation. These sources were low radiation sources that do not require a license.

2.1.2 Results

The investigators had hoped to demonstrate the use of broad energy radiation sources and unique absorption profiles to identify specific concrete mix constituents on the basis of their mineralogy. However, this was not the case.

Figure 12 shows the spectrum of energy transmitted through a sample of air, water, and cement paste (water-cement mixture). The sample thickness was approximately 1.5-inches. These data revealed that the gamma radiation was predominately absorbed at lower energies (below 100 keV).

These data clearly show that by examining the peak at 25 keV, one can easily characterize the relative density of the samples by their relative attenuation of the gamma radiation. Additional

analysis was performed at lower energies. The lower-energy data showed a large amount of Compton scattering. However the investigators were unable to determine if this scatter was taking place in the sample itself or in the detector (thereby making the value of those data questionable).

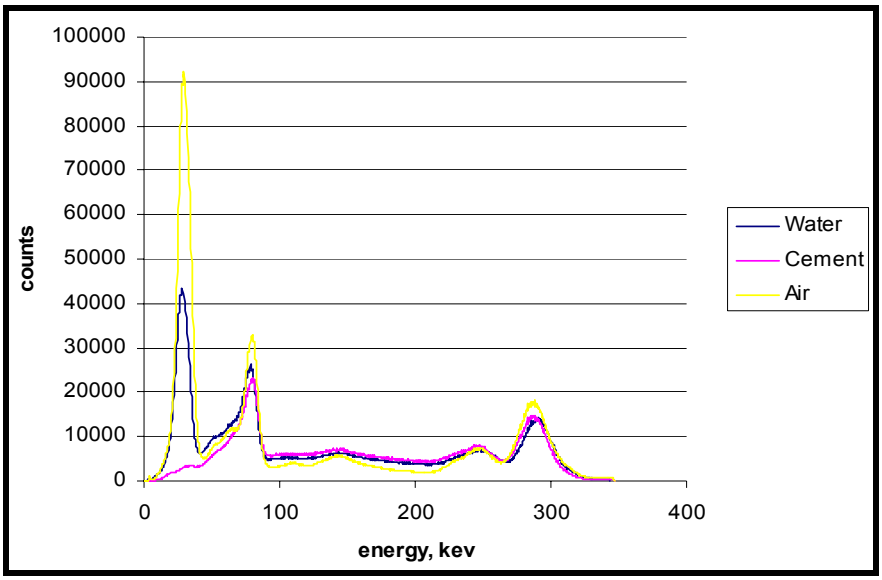

Figure 12 – Gamma Radiation Absorption for Water, Cement, and Air

2.2 Preliminary Evaluation: Fluorescence & Standard Addition (FSA)

Continuing with the preliminary evaluation, the investigators evaluated a fluorescence method in conjunction with the standard addition technique for quantifying *W/C*.

The fluorescence method, based on ASTM C1079, involves fresh concrete being intermixed with a chloride solution of a given strength and volume. The chloride solution mixes with the free water in the concrete. The chloride ion concentration of the intermixed solution is directly related to the water content of the concrete sample and is determined by volumetric titration or coulometric reference techniques. Since some concretes contain chlorides, determining the effect of the additional chloride ions can be a challenge. One method of overcoming this problem is via standard addition – in which the effect of subsequent additions of chloride ions are analyzed to determine the incremental change in concentration, thus yielding the amount of free water in the specimen.

The challenge facing the investigators was to find a similar method involving the addition of a chemical that does not typically exist in concrete, and then being able to accurately determine the amount of dilution induced by the free water in the specimen.

2.2.1 Theory

Due to matrix effects, the analytical response for an analyte in a complex sample may not be the same as for the analyte in a simple standard. In this case, calibration with a working curve would

require standards that closely match the composition of the sample. For routine analyses it is feasible to prepare or purchase realistic standards, e.g. NIST standard reference materials. For diverse and one-of-a-kind samples, this procedure is time consuming and often impossible.

An alternative calibration procedure is the standard addition method. An analyst usually divides the unknown sample into two portions, so that a known amount of the analyte (a spike) can be added to one portion. These two samples, the original and the original plus spike, are then analyzed. The sample with the spike will show a larger analytical response than the original sample due to the additional amount of analyte that has been added to it.

The difference in analytical response between the spiked and non-spiked samples is due to the amount of analyte in the spiked sample. This provides a calibration point to determine the analyte concentration in the original (non-spiked) sample.

2.2.2 Approach

The investigators performed a series of mini-experiments on this concept using rhodamine, a fluorescent die that is never present in concrete, relatively nontoxic, low cost, and generally does not "stick" to solid materials. When rhodamine is optically excited at a wavelength of 560 nm, it emits the emission spectrum shown in Figure 13.

The intensity is directly proportional to concentration up to approximately 1 ppb. Above 1 ppb the dye self-quenches. The relationship at the low ppm level is linear, as shown in Figure 14, and therefore most useful.

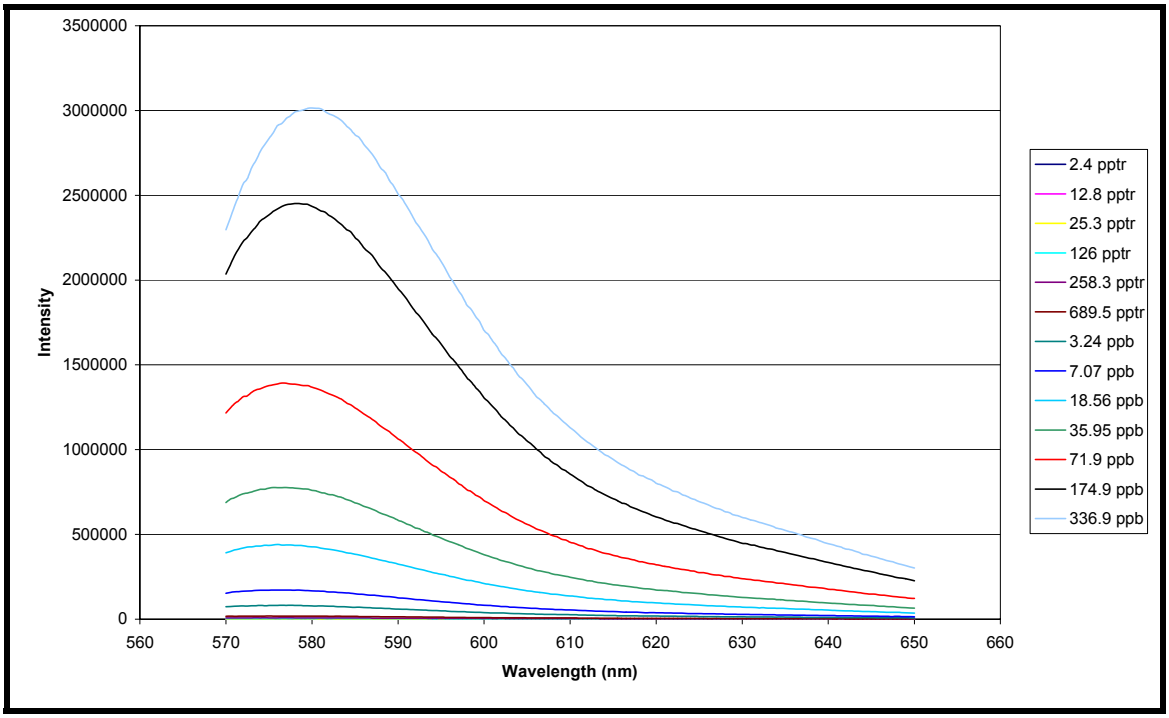

Figure 13 – Emission Spectrum for Rhodamine at 560 nm Excitation

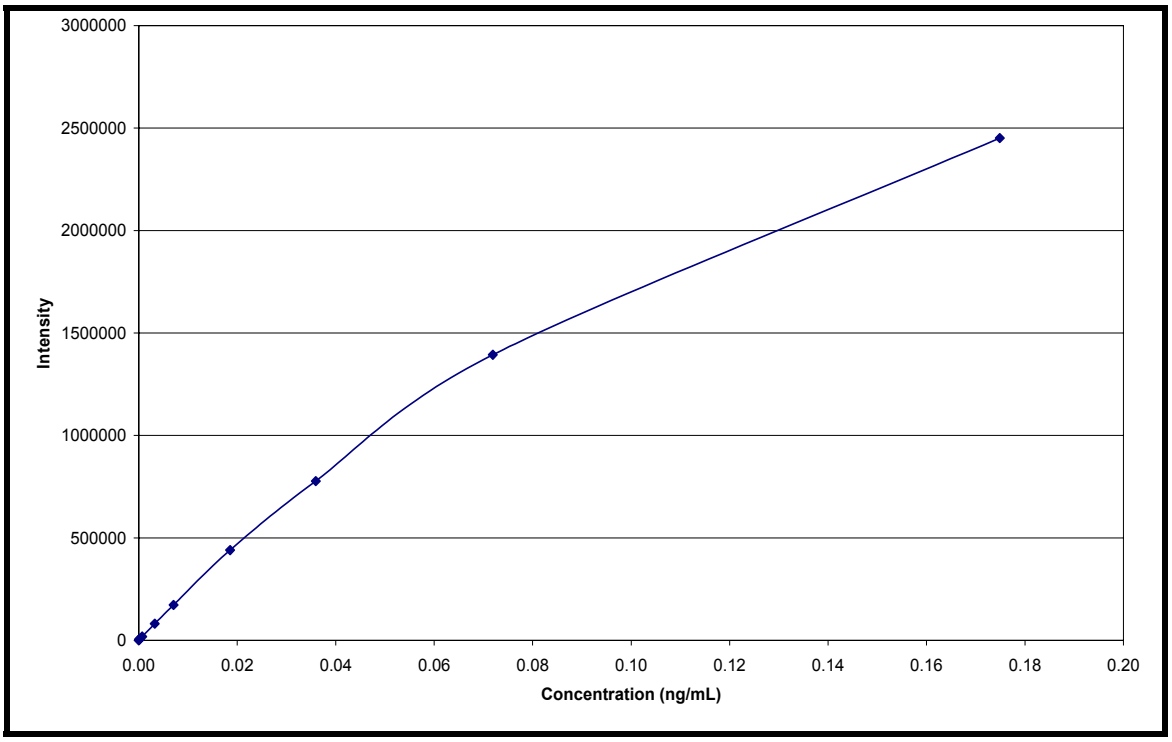

Figure 14 – Emission Intensity of Rhodamine as a Function of Concentration

2.2.3 Emission Stability

One concern regarding fluorescence measurement is the stability of the fluorescence in the presence of an unpredictable environment. The two key potential interfering parameters are temperature and pH. The investigators therefore tested the stability of the dye under varying conditions. The influence of temperature and pH on fluorescence intensity is shown in Figure 15 and Figure 16, respectively.

The dye has a temperature coefficient of 2% per degree-C. This temperature coefficient is not an insurmountable problem; however, an instrument for this application would have to be designed to correct for the variation. This can be done by several techniques ranging from simple mathematical compensation, to more complex dual-beam designs. A more serious concern for this approach was the stability of the dye in a high pH medium. The pH sensitivity graph (Figure 16) shows that the dye is quite stable at elevated pH values. This is a very beneficial fact considering the extremely high pH values present in fresh concrete.

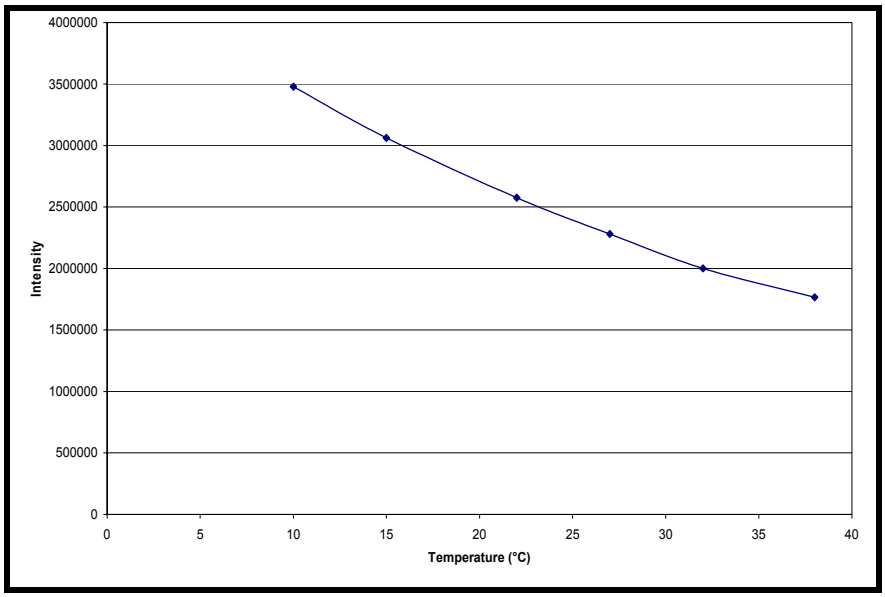

Figure 15 – Emission Intensity of Rhodamine as a Function of Temperature (at 174 ng/mL)

2.2.4 Procedure and Results

To test this technique, the investigators used standard addition methodology utilizing dye fluorescence as the indicator of dye concentration. The basis for this technique is that first the specimen of fresh concrete is dyed, then subsequently diluted. The incremental change in fluorescence from a known dilution of the dye is indicative of the initial amount of water present.

Several procedures were performed with an initial specimen of water only (no other concrete components) to test the viability of this technique using fluorescence as in indicator of free water. The investigators were able to determine the initial amount of water in the specimen, even when the specimen varied in pH. However, when the process was repeated with additional concrete components, such as cement and aggregates, the results were inconsistent.

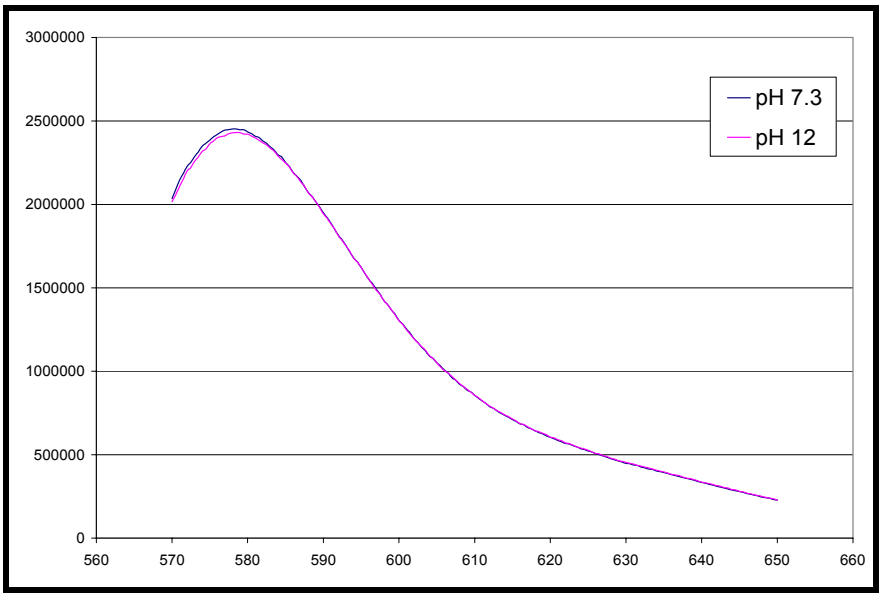

Figure 16 – Emission Intensity of Rhodamine as a Function of pH

Subsequent procedures were performed in which cement, sand, and coarse aggregate were added to a dyed and agitated sample. The results suggest that the dye is being partially adsorbed due to the high surface area of the solids in the specimen. The table below shows the fluorescence intensity in each of the samples as a percentage of the theoretical (expected) value.

Sand	68%
Coarse Aggregate	54%
Cement	41%

This result was unexpected considering the fact that rhodamine is routinely used as an aqueous dye because it typically does not adsorb onto solid components. This procedure has limited value in this application until this problem can be overcome. However, this technique could prove promising as a means to measure the specific surface of the concrete's constituent materials. Specific surface as a quality control parameter is becoming more and more important as concrete suppliers begin to move toward optimized-gradation mix designs and self-consolidating concrete mixes, both of which require strict control on the size distribution of the solid materials in the mix.

2.3 Preliminary Evaluation: Specific Gravity (or Unit Weight)

The investigators began this preliminary evaluation by examining the *Specific Gravity* (or *Unit Weight*) method. This method relies on a series of equations shown below that can be simplified to reveal four unknowns. The investigators then developed several mini-experiments to measure these unknowns.

2.3.1 Derivation of the Underlying Equations

The density of concrete equals the mass of all the constituents per the volume of all the constituents, or on a weight basis by multiplying each side by gravity:

$$\rho_{conc} = \frac{m_{conc}}{V_{conc}} = \frac{m_{water} + m_{cement} + m_{agg}}{V_{water} + V_{cement} + V_{agg}} = \frac{W_{water} + W_{cement} + W_{agg}}{\frac{W_{water}}{\rho_{water}} + \frac{W_{cement}}{\rho_{cement}} + \frac{W_{agg}}{\rho_{agg}}} \quad \text{Equation (1)}$$

Note that the volumetric amount of air was intentionally left out of the equation since the air is removed before any measurements are taken.

The specific gravity of the concrete equals the density of the concrete (Equation 1) divided by the density of water. Dividing both sides of Equation 1 by the ρ_{water} yields the following:

$$\gamma_{conc} = \frac{W_{water} + W_{cement} + W_{agg}}{\frac{W_{water}}{\gamma_{water}} + \frac{W_{cement}}{\gamma_{cement}} + \frac{W_{agg}}{\gamma_{agg}}} \quad \text{Equation (2)}$$

Solving Equation 2 for W_{water} / W_{cement} (or *W/CM*) yields the following:

$$W/CM = \frac{W_{water}}{W_{cement}} = \frac{\left(1 - \frac{\gamma_{conc}}{\gamma_{cement}}\right) + \frac{W_{agg}}{W_{cement}}\left(1 - \frac{\gamma_{conc}}{\gamma_{agg}}\right)}{\gamma_{conc} - 1} \quad \text{Equation (3)}$$

Whereas $\gamma_{concrete}$ can be defined as the weight of the concrete divided by the weight of water displaced by the concrete, the method of water-displacement can be used to determine $\gamma_{concrete}$ as follows:

$$\gamma_{concrete} = \frac{W_{concrete}}{W_{water-displaced-by-concrete}} \quad \text{Equation (4)}$$

As such, a volumetric container can be used to measure $\gamma_{concrete}$ by taking the following four mass (or weight) measurements – the container empty, the container full of water, the container with the concrete sample only, and the container with the concrete sample subsequently filled with water. Equation 5 below shows the calculation for specific gravity from these four measurements:

$$\gamma_{concrete} = \frac{W_{concrete-in-container} - W_{empty-container}}{W_{water-filled-container} - W_{empty-container} - W_{concrete-and-water-filled-container}} \quad \text{Equation (5)}$$

Symbols

γ = Specific Gravity
ρ = Density
m = Mass
W = Weight
V = Volume
W/CM = Water-to-Cementitious-Materials Ratio

Subscripts

agg = Aggregate
cement = Cement or Cementitious Materials
conc = Concrete

water = Water

Note that "cement" or "cementitious" refers to the net weight and/or density of all the cementitious materials in the mix (e.g. cement and fly ash). Similarly, "aggregate" refers to the net weight and/or density of all the aggregate materials in the mix (e.g. coarse and fine aggregate).

As shown by Equation 3 above, the water-to-cementitious-materials ratio (*W/CM*) can be determined without bias and without assumption if the following parameters are accurately and precisely known (or measured):

- Specific gravity, or unit weight, of the fresh concrete (γ_{conc})
- Net specific gravity of the aggregates (γ_{agg}). This requires the following:
  - Individual specific gravities of each aggregate source, and
  - The relative proportions of each aggregate source. (NOTE: These numbers can typically be obtained from the batch tickets, but with uncertain reliability due to the unknown amount of moisture in the aggregates.)
- Net specific gravity of the cementitious materials (i.e. cement and fly ash) (γ_{cement}). This requires the following:
  - Individual specific gravities of the cement and fly ash, and
  - The relative proportion of fly ash to cement. (NOTE: This number can usually be reliably obtained from the batch ticket.)
- Cementitious-materials-to-aggregate ratio (W_{cement} / W_{agg}, or *CM/A*)

NOTE: Whereas previous attempts by other researchers to precisely measure *W/CM* have encountered specific difficulties related to the coarse aggregates (e.g. due to the different porosity and absorption characteristics of various coarse aggregate sources), the investigators employed a sampling and testing procedure that effectively removes the coarse aggregate portion of the mix, thus leaving a mortar-only specimen for the actual *W/CM* test. The preferable nature of this approach is apparent when one considers that any water that may be present in the aggregates (i.e. *not* present in the paste) should *not* be included in the *W/CM* measurement. Therefore, removal of larger aggregates from the analysis will tend to improve the precision of the final *W/CM* measurement. As such, the concrete specific gravity values discussed herein will be those of the concrete minus the coarse aggregates (with all entrained and entrapped air removed as well). Also, the specific gravity of the aggregates will be the specific gravity of the sand. As such, the cementitious-materials-to-aggregate ratio (*CM/A*) will be replaced with the cementitious-materials-to-sand ratio (*CM/S*).

Whereas the specific gravities of the individual components tend to remain fairly constant (provided the raw material sources are constant), the investigators focused on the remaining parameters (concrete specific gravity, *CM/S*, and *F/CM*). However, the investigators anticipate that the final device for measuring *W/CM* via specific gravity would also be able to separately measure the specific gravities of individual raw materials (to function as a validation for the *W/CM* measurements, and also to serve as a quality-control check on the raw materials themselves).

2.3.2 Performing Specific Gravity Mini-Experiments

The overall mixture design experiment was performed based on three mixture variables (water, sand, and cementitious materials) and one process variable (fly ash replacement percentage, or *F/CM*). A total of thirty-three different treatment combinations were tested, three of which were replicated, for a total of thirty-six different specimens. For each specimen, concrete specific gravity, *CM/S*, and *F/CM* were measured and compared back to the actual values as described below.

Although unit weight of concrete is a commonly-measured parameter, the true benefits of concrete unit weight measurements have been inappreciable due to the lack of precision of the current standard procedure (ASTM C138). This lack of precision is primarily due to the inaccuracy of the volumetric measurement (which involves a technician consolidating the concrete into a fixed-volume container, then weighing the container). Water displacement, as opposed to the fixed-volume technique of C138, is a more accurate technique.

To measure the unit weight, or specific gravity, of the concrete, the investigators utilized water displacement in a pycnometer with the following procedure:

1. Weigh the pycnometer full of water.
2. Weigh the pycnometer empty.
3. Add the fresh concrete to the pycnometer.
4. Weigh the pycnometer with the fresh concrete.
5. Fill the remainder of the pycnometer with water.
6. Agitate the pycnometer to remove all air from the concrete.
7. Top off the pycnometer with water.
8. Weigh the pycnometer full of concrete and water.

Steps 1 and 2 enabled the investigators to determine the volume of the pycnometer. Step 4 provided the weight of the concrete. Step 8 (in conjunction with Steps 1 and 2) provided the volume of the concrete, and thus the specific gravity (or unit weight) of the concrete. Also, since the pycnometer is calibrated with water at the beginning of the procedure (for each specimen), the procedure provides a *true* specific gravity measurement. This is because the density of the water is included in the measurement and thus does not need to be assumed.

With respect to the cementitious-materials-to-sand ratio, or *CM/S*, the investigators observed that the human eye can very easily distinguish differences in *CM/S* by simply placing a mortar specimen into a mason jar, shaking the jar vigorously, then allowing the mixture to settle by natural sedimentation. Figure 17 demonstrates this effect with mixtures having *CM/S* ratios of 0.0, 0.1, 0.2, 0.3, and 0.4 (from left to right). The differences from specimen to specimen are clearly observable.

Figure 17 – Visual Demonstration of Different Cementitious-Materials-to-Sand Ratios (*CM/S*)

In light of this observation, the investigators developed a standard sedimentation procedure for determining *CM/S* (to be performed on each specimen immediately after the specific gravity of the specimen was determined, as described above). The sedimentation procedure involved placing the specimen into a sedimentation chamber consisting of a household pitcher equipped with a manual stirrer (as depicted in Figure 18). After additional water was added to the specimen, the stirrer was mobilized to agitate the diluted specimen, thus creating a homogenous suspension. The stirring was then abruptly halted, causing the sand particles to immediately drop to the bottom of the sedimentation chamber. The cementitious materials would settle also, albeit much more slowly than the sand particles. Digital images of the settling sand and cementitious materials were taken and analyzed to determine the relative heights of the sand column and the cementitious-materials column (which were then compared back to the actual cementitious-to-sand ratios). Figure 18 shows a typical specimen in the sedimentation column. Color measurements of the cementitious layer and the sand layer were also analyzed to determine the fly ash replacement percentage, or *F/CM*, of the mix.

As mentioned above, the investigators conducted a mixture design experiment using the aforementioned procedures in an effort to determine how well these concepts can be used to measure the desired parameters. To accomplish this task, the investigators intentionally varied the mixture constituents across a broad range (so that the statistical significance of the individual measurement systems could be clearly determined). Statistical analysis of the results demonstrated that each of the chosen measurement systems is highly significant in explaining the observed variability of each desired parameter (concrete specific gravity, *CM/S*, and *F/CM*) across the mixtures evaluated ($p < 0.001$ in all cases).

The coefficient of determination (R^2) for the concrete specific gravity measurements was 99.9%, meaning that 99.9% of the variability in actual concrete specific gravities could be explained (i.e. measured) by the eight-step procedure described above. Figure 19 shows the associated regression line and prediction equation for measured versus actual specific gravity (with 95% confidence intervals shown in red and 95% prediction intervals shown in blue). Similarly, the *CM/S* measurement procedure was able to explain 96% of the variability in actual *CM/S* values

(see Figure 20) and the *F/CM* procedure captured 90% of the variability of actual *F/CM* (see Figure 21).

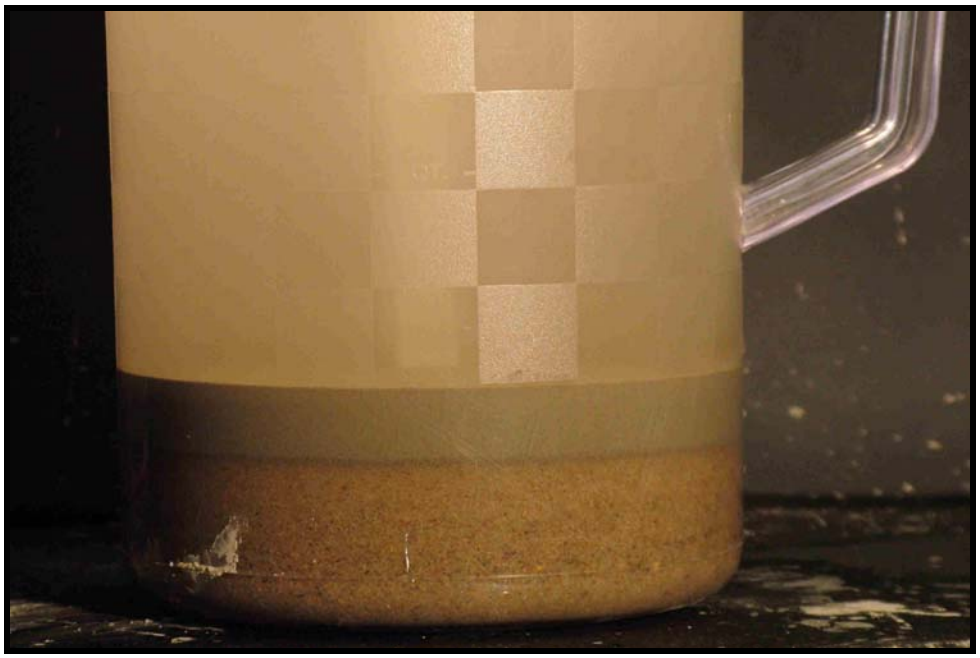

Figure 18 – Sedimentation Chamber for Measuring Cementitious-Materials-to-Sand Ratio (*CM/S*)

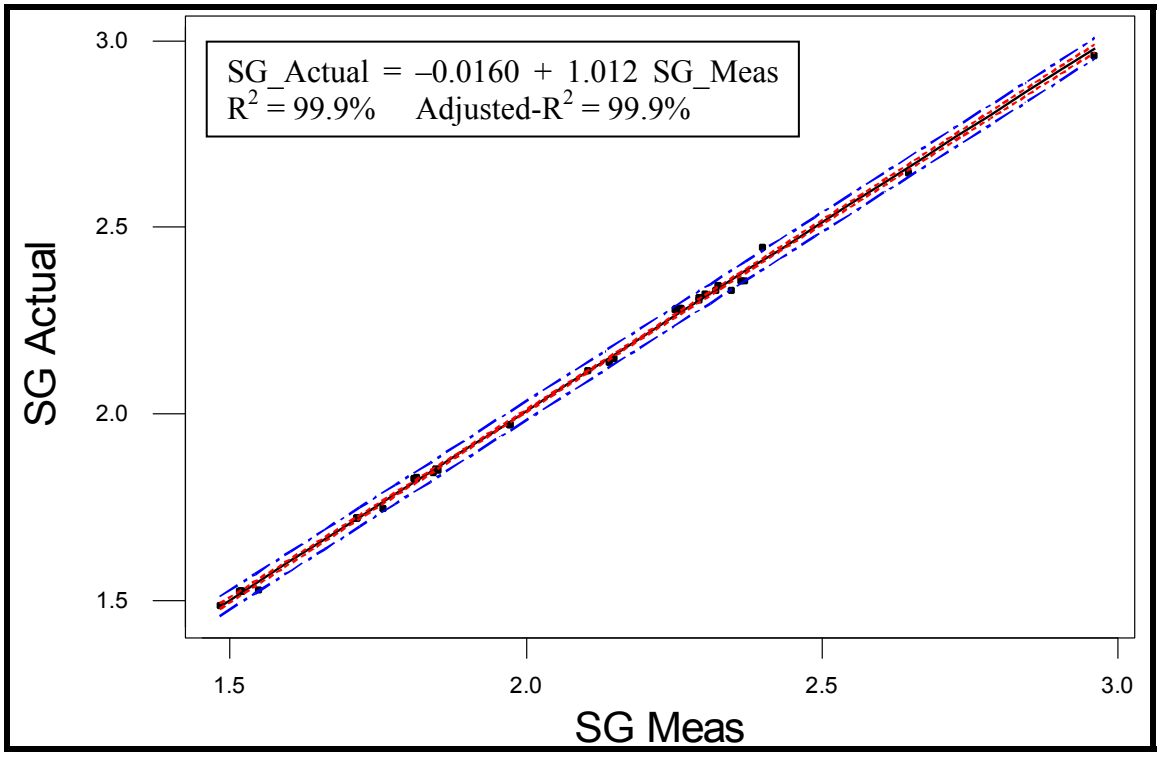

Figure 19 – Regression Analysis of Measured versus Actual Concrete Specific Gravity

The investigators were extremely pleased that the coefficient of determination for the concrete specific gravity measurement was so high (99.9%) considering the fact that the weight measurements for the relatively small specimens were performed using a 150-pound-capacity scale (i.e. the specimen weight measurements were taken at less than 2% of the full-scale range of the weighing instrument).

Similarly, the procedures implemented for the measurements of *CM/S* and *F/CM* were less than optimal, thus leaving considerable potential for improved precision with the final device. For example, the height-to-diameter ratio (*h/d*) of the sediment column for the *CM/S* measurement was much less than one. An ideal *h/d* would be much greater than one. Also, the lighting conditions for the *F/CM* measurements were not constant across the front of the sedimentation column. This can be seen clearly in Figure 22, which shows the relative RGB light intensity (red, green, and blue) of the pixels from left to right across the cement column of one of the specimens. This change is due to the curved nature of the sediment chamber. An ideal setup would utilize a chamber having a flat front surface within a tightly controlled lighting environment (such as in a sealed compartment).

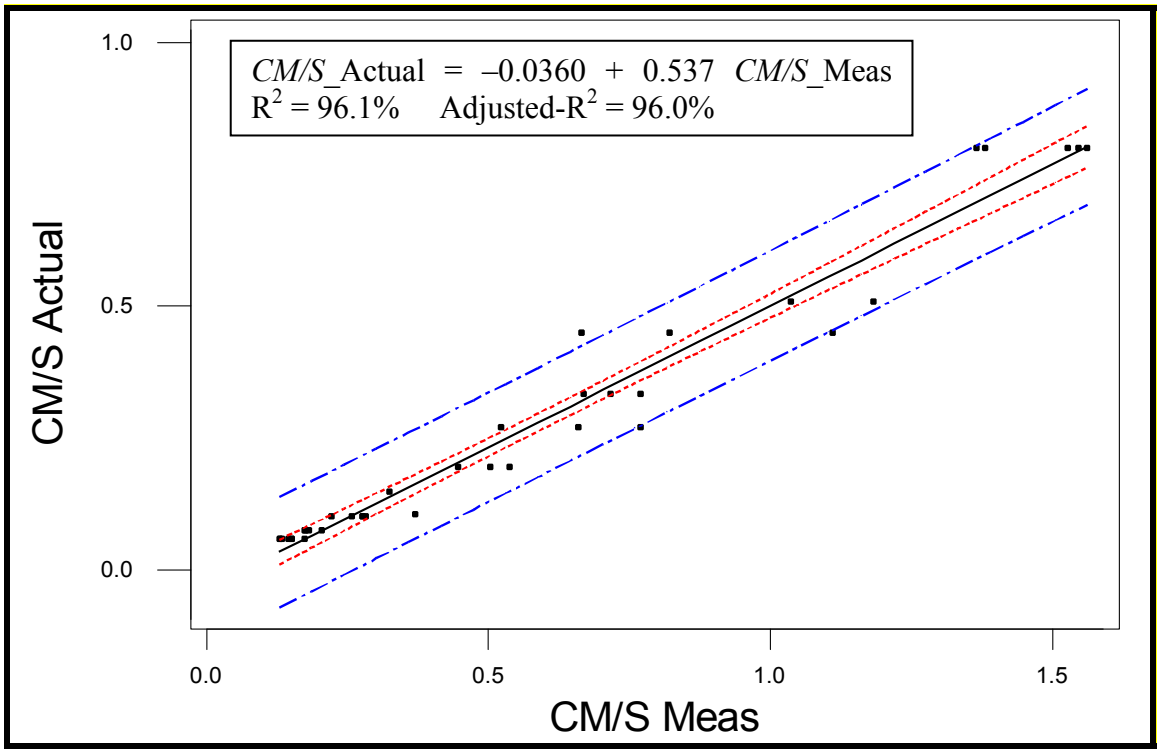

Figure 20 – Regression Analysis of Measured versus Actual Cementitious-Materials-to-Sand Ratio (*CM/S*)

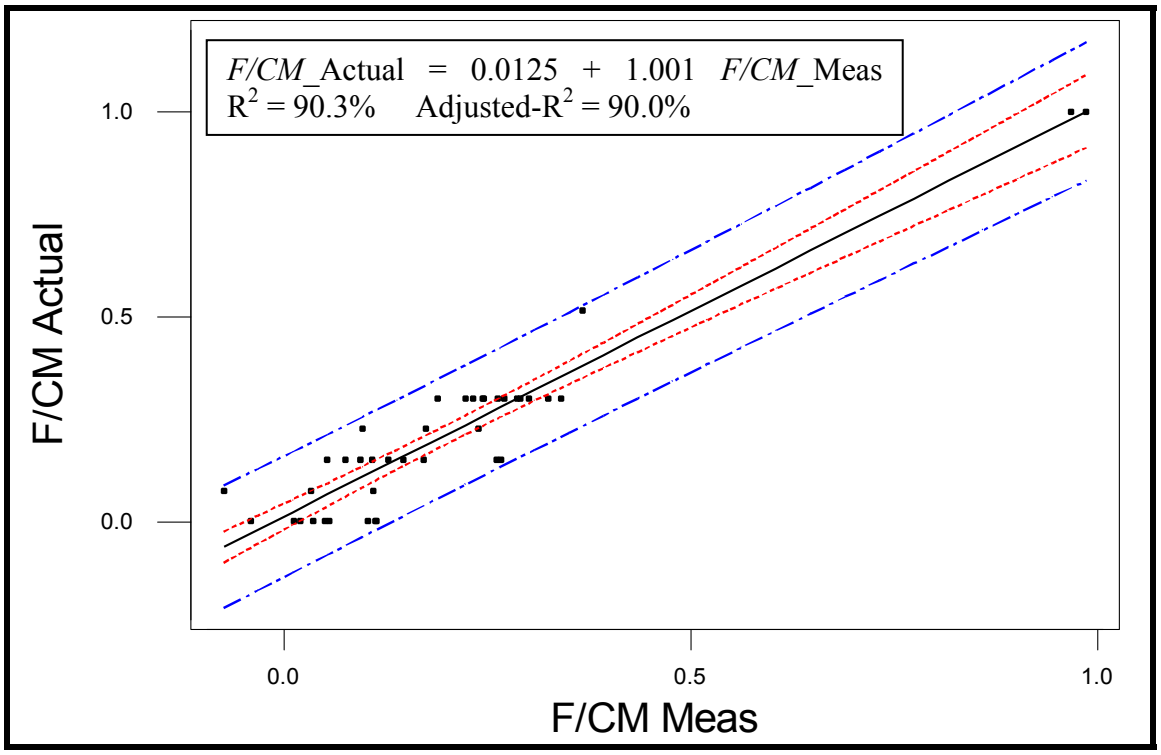

Figure 21 – Regression Analysis of Measured versus Actual Fly Ash Replacement Percentage (*F/CM*)

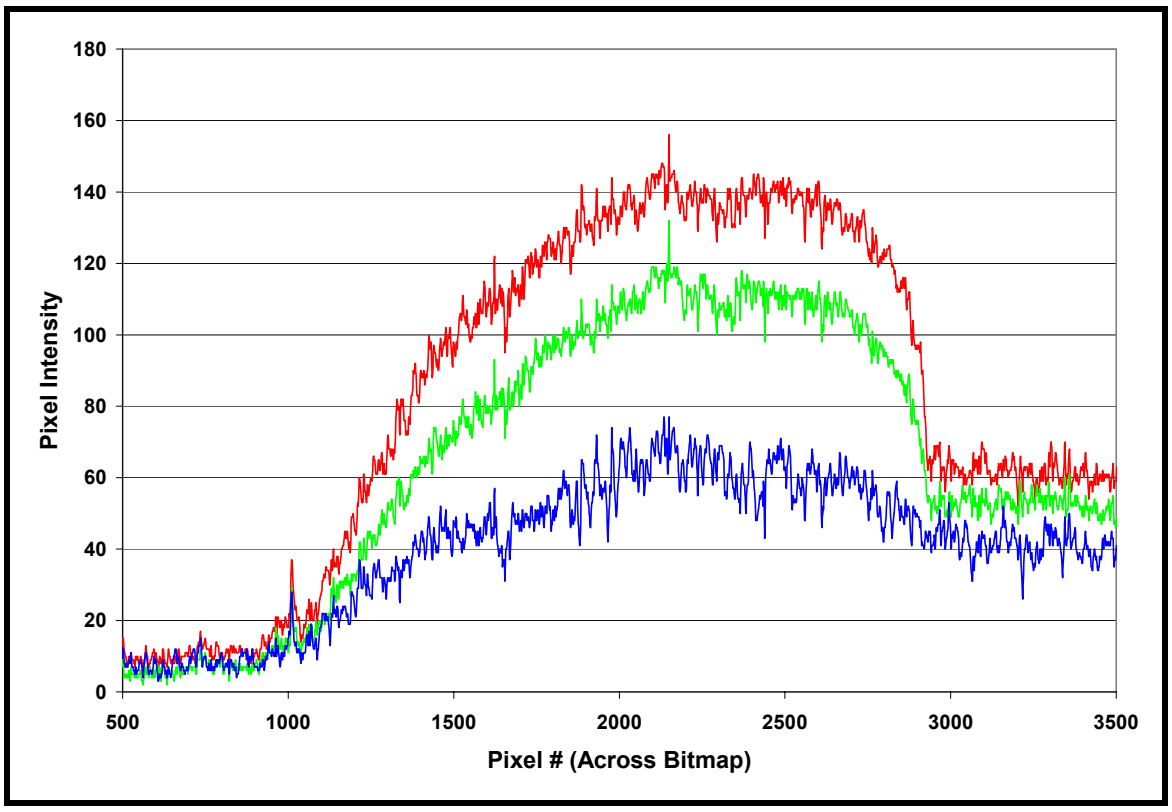

Figure 22 – Relative RGB Light Intensity across Cement Column in Sedimentation Chamber (Left to Right)

2.4 Preliminary Evaluation: Microwave-Oven-Drying

The investigators also examined previous research on the *Microwave-Oven-Drying* method for calculating *W/C*. However, no preliminary evaluation testing was initially performed for this method.

2.4.1 Background

Various studies have been conducted evaluating the effectiveness of the *Microwave-Oven-Drying* method for determining the water content of fresh concrete (Tom and Magoun 1986, Nagi and Whiting 1994, Dowell and Cramer 2002). The studies conducted by U. S. Army Corps of Engineers Waterways Experiment Station (WES) (Tom and Magoun 1986) on the *Microwave-Oven-Drying* method yielded a pooled coefficient of variation (COV) of 7.7% for water content and 4.5% for *W/CM* (using actual batch weights for cementitious materials). However, these values were based on one "test result" being the average of five individual measurements. As such, the respective single-test COVs can be estimated by the central limit theorem to be 17.3% and 10.1%. In practical terms, a 10% COV means that if the measured *W/CM* is 0.50, the actual value can be expected to fall between 0.40 and 0.60 (with 95% confidence).

A study conducted by the Wisconsin Highway Research Program (Dowell and Cramer 2002) reported a standard error equal to 0.03 when using the *Microwave-Oven-Drying* method to measure *W/CM* of concrete paving mixes having an average *W/CM* of 0.35. This equates to a COV of 8.6%, which is only slightly better than the values obtained by WES in the 1980s.

Halstead (1993) reported that the major difficulties associated with the *Microwave-Oven-Drying* method were:

1. Difficulty obtaining a representative sample,
2. Accounting for the absorbed water in the aggregate,
3. Accounting for evaporable liquid in liquid admixtures,
4. Decomposition of aggregate particles during heating, and
5. Popping of aggregate particles during heating resulting in loss of sample material.

In an attempt to account for Difficulty #2, the Indiana Department of Transportation (InDOT) developed a correction factor to adjust or "correct" the measured water content based on the amount of coarse aggregate in the sample. However, when the WHRP researchers applied the InDOT correction factor to their data, the results were questionable. In fact, WHRP reported that after applying the correction factor, "the corresponding standard errors increased for most jobs." (Dowell and Cramer 2002)

3. FURTHER EVALUATION OF SPECIFIC GRAVITY & TURBIDITY METHODS

Based upon the preliminary evaluation of different methods for quantifying *W/C*, the investigators believed that the *Specific Gravity* method had shown the most promise. The investigators decided to implement a turbidity measurement in conjunction with specific gravity to measure cement content as well as *W/C*.

The investigators also decided to develop an automated specific-gravity device that would improve the precision of the method's volumetric measurements by reducing user interaction.

3.1 Developing an Automated Specific-Gravity Measurement Device

The investigators developed an automated system for measuring specific gravity based on equations described in Section 2.3.1. The system, shown in Figure 24, comprises the following:

- Precision scale with digital indicator (2 kg capacity / 0.025 g resolution),
- Volumetric pycnometer container (1 ℓ capacity) with automated fill mechanism
    - Overflow gate (to accommodate automated filling with replicate sampling),
    - Laptop computer with custom software (auto-fill control, user-interface, step-by-step user instructions),
    - Computer-actuated auto-fill control valve,
    - Electronic interface between computer, scale, and control valve.

The user interface provides on-screen instructions guiding the user through the following steps (the four steps in **bold** are performed by the user; the eleven steps in *italics* are automatically performed by the system):

1. *Zero the scale,*
2. **Place the empty container on the scale,**
3. *Record the mass of the container (empty),*
4. *Fill the empty container with water,*
5. *Record the mass of the container (filled with water),*
6. *Repeat Steps 4 and 5 multiple times (replicate sampling) and record the average value,*
7. **Empty the container and place the empty container on the scale,**
8. *Record the mass of the empty container,*
9. **Place the concrete sample in the container and place the container on the scale,**
10. *Record the mass of the container (with the concrete sample),*
11. *Fill the container 3/4 full with water,*
12. **Agitate the container to remove any entrapped or entrained air from the concrete sample and place the container on the scale,**
13. *Fill the remainder of the container with water,*
14. *Record the mass of the container (with the concrete sample and water),*
15. *Repeat Steps 12 and 13 multiple times (replicate sampling) and record the average value.*

Extensive testing on this automated system was made using a wide range of mixtures and *W/CMs*. Results showed that this system could consistently measure volume with a standard error of only 0.12%.

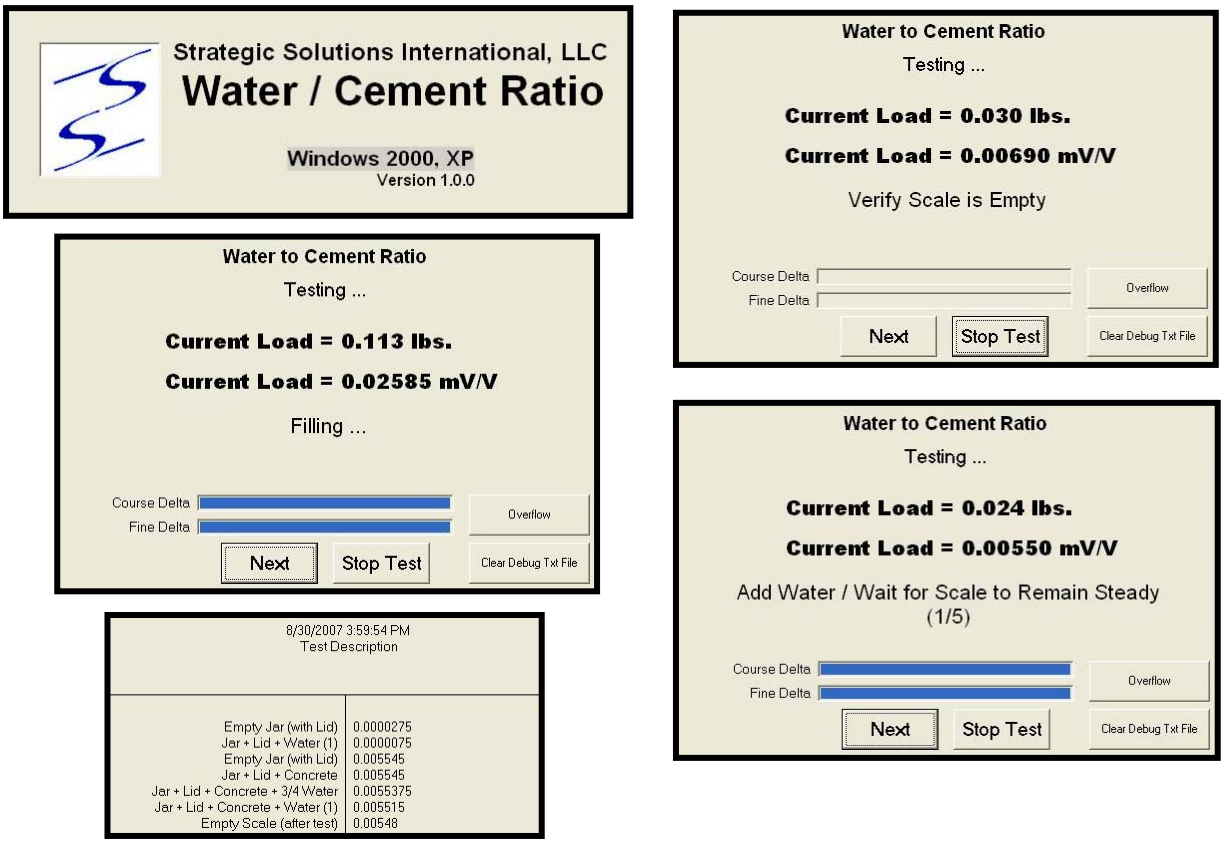

Figure 23 – Screen Shots of Control Software for Automated Specific-Gravity Measurement System

Figure 24 – Photographs of Automated Specific-Gravity Measurement System

3.2 Modified Procedure & Results

In addition to the Automated Specific-Gravity Measurement Device, the investigators made the following changes to the preliminary evaluation testing procedure:

- The *h/d* ratio of the sedimentation chamber used for measuring *CM/S*, as seen in Section 2.3.2, was changed from 0.5 to 2.5.
- A turbidimeter with a measurable range of 0 to 30,000 NTU was acquired and used to measure cement content.
- A cementitious materials chamber was implemented as an additional measurement of cement or cementitious materials content.
- Fine and coarse aggregates were screened, and specific gravity calculations were made for each aggregate.

The modified procedure contained a total of seven mini-experiments. By testing with more mini-experiments, the investigators hoped to find the most efficient combination for precisely quantifying *W/C*. Four concrete batches (representing the four ways in which *W/C* varies) were mixed, and a total of twenty-four specimens were tested.

Figure 25 shows the regression line of calculated versus measured specific gravities for the tested specimens. As can be seen, the results demonstrate very good capability with the process of measuring specific gravity in accordance with Equation 5, with a coefficient of determination (R^2) of 99.87% and a standard error of 0.77%.

Figure 26 shows the regression line and data of calculated versus measured water-to-cementitious-materials ratio (*W/CM*) using the specific gravity measurements from Figure 25 in conjunction with reported batch values for the mass of aggregates and cementitious materials.

The results of Figure 26 show that the predictive capability of *W/CM* using the *Specific Gravity* method (for concrete mixes) yielded an R^2 = 98.85% and a standard error = 6.9%. Thus, for a *W/CM* of 0.50, the actual *W/CM* can be expected to fall in between 0.43 and 0.57 (with 95% confidence). These results demonstrate better precision than those of existing *W/CM* methods for fresh concrete but represented a reduction in precision from the preliminary evaluation (which used mortar mixes only) (see Section 2.3.2). The investigators believe that the decrease in precision was due to the increase in the number of experimental variables. However, the results from the second evaluation are more representative of what could reasonably be expected when using the *Specific Gravity* method to measure the *W/CM* of fresh concrete.

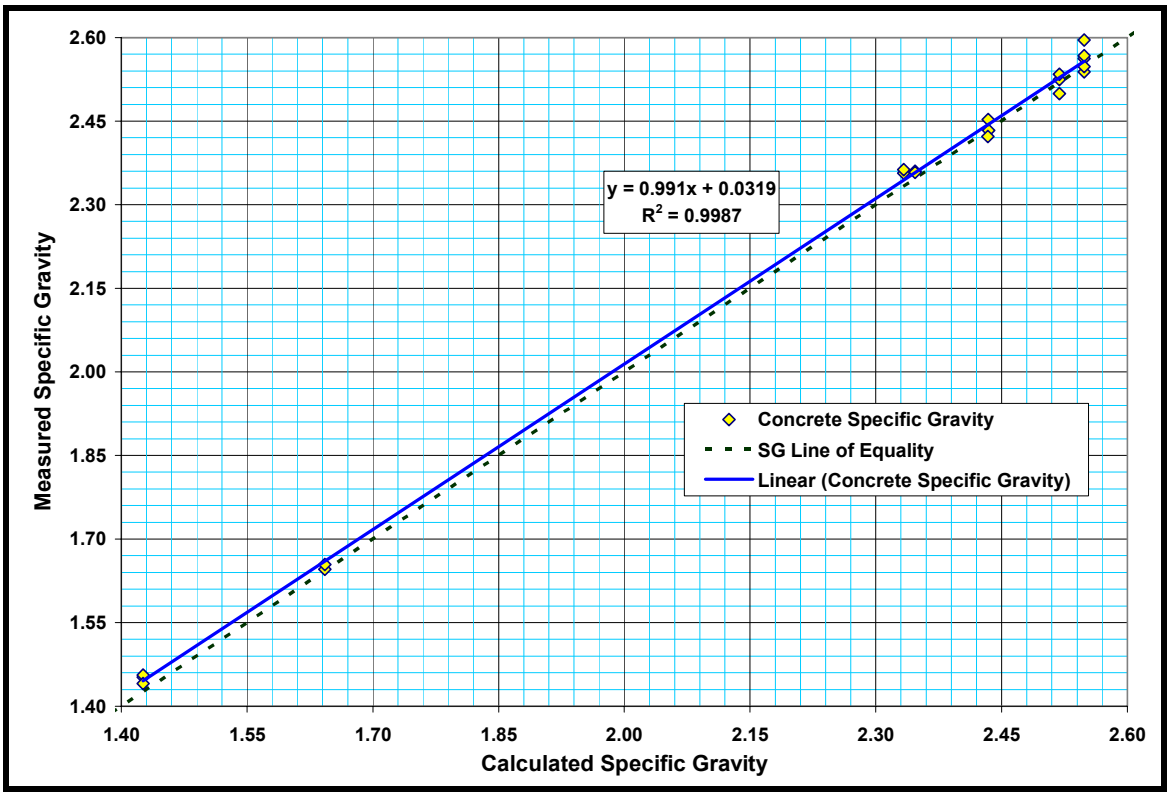

Figure 25 – Regression Line of Calculated versus Measured Specific Gravity

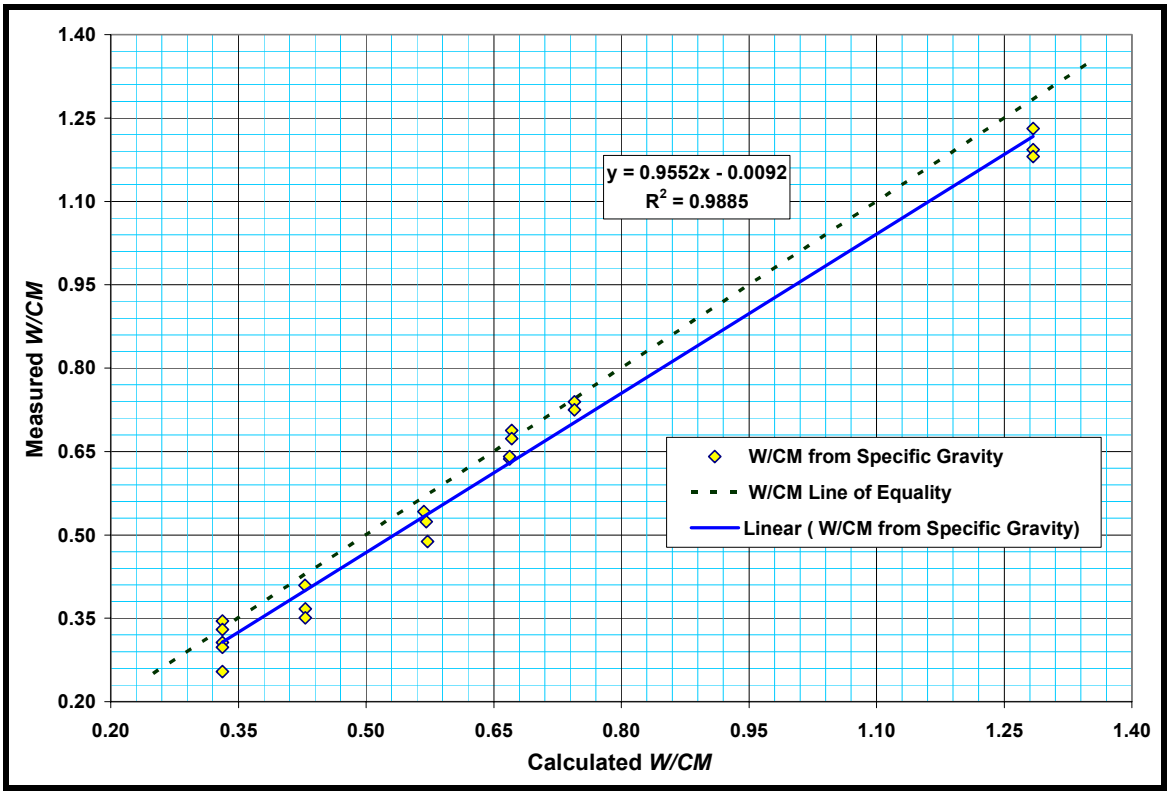

Figure 26 – Regression Line of Calculated versus Measured *W/CM* (using Specific Gravity)

4. PASTE EXTRACTION METHOD USING TURBIDITY

After a careful re-evaluation of the *W/CM*-from-turbidity concept, the investigators realized that the very issue that promulgated errors in previous researchers' validation of the Kansas device could actually be used to enhance the feasibility of turbidity as a viable method to measure water-to-cementitious-materials ratio (*W/CM*). The root cause of the earlier errors was the fact that with mixture designs, the experimenter cannot change only one parameter (as discussed in Section 1.3.1). As such, at least two components must change every time the mixture is adjusted. However, this "problem" with mixtures has a very interesting side effect – if only two components are included in the mixture (i.e. a *binary* mixture), changing one by definition changes the other. As such, if a multi-component mixture can be somehow reduced to a binary mixture, only one of the two components need be measured.

In other words, if a concrete sample can be effectively reduced to a "paste-only" specimen (i.e. containing only cement and water), then measuring the cement content will effectively confirm the water content (and thus the *W/CM*). And, whereas turbidity has been shown to be an effective method for measuring cement mass in a concrete (or paste) sample, turbidity may be able to effectively measure the *W/CM* of fresh concrete.

Based on this realization, and to test their hypothesis, the investigators used the newly-acquired turbidimeter (see Section 3.2) and developed a system for extracting paste from samples of fresh concrete. The new, high-range turbidimeter was used to verify the high sensitivity of turbidity to the mass of cement in a sample of paste and the very low sensitivity of turbidity to the mass of water in a sample. With the 30,000 NTU device, the sensitivity of turbidity measurements to cement was found to be Cement = NTU / 7814.7 (where "Cement" represents the mass of cement in pounds when dispersed into 30 pounds of water). The correlation between NTU and Cement Mass is shown in Figure 27, where the diamonds represent the steady addition of cement to 30 pounds of water and the circles represent successive dilutions of the diluted-paste mixture (wherein portions of the mixture were removed and subsequently replaced with an equal volume of clear water, leading to a subtraction in the total cement mass).

The paste-extraction system utilized high-frequency vibration (~ 11,000 vpm) and an ultra-fine screen (screens tested ranged from 35 to 125 μm). Initial results with the paste extraction device were promising. However, the investigators experienced difficulty in consistently extracting paste from relatively dry concrete mixes (i.e. *W/CM* less than 0.45). This was primarily due to clogging of the screens by the moist cement particles. However, increasing the screen size resulted in contamination of the "paste only" sample with fine aggregate fines. As such, the investigators did not find this method presently worthy of additional investigation.

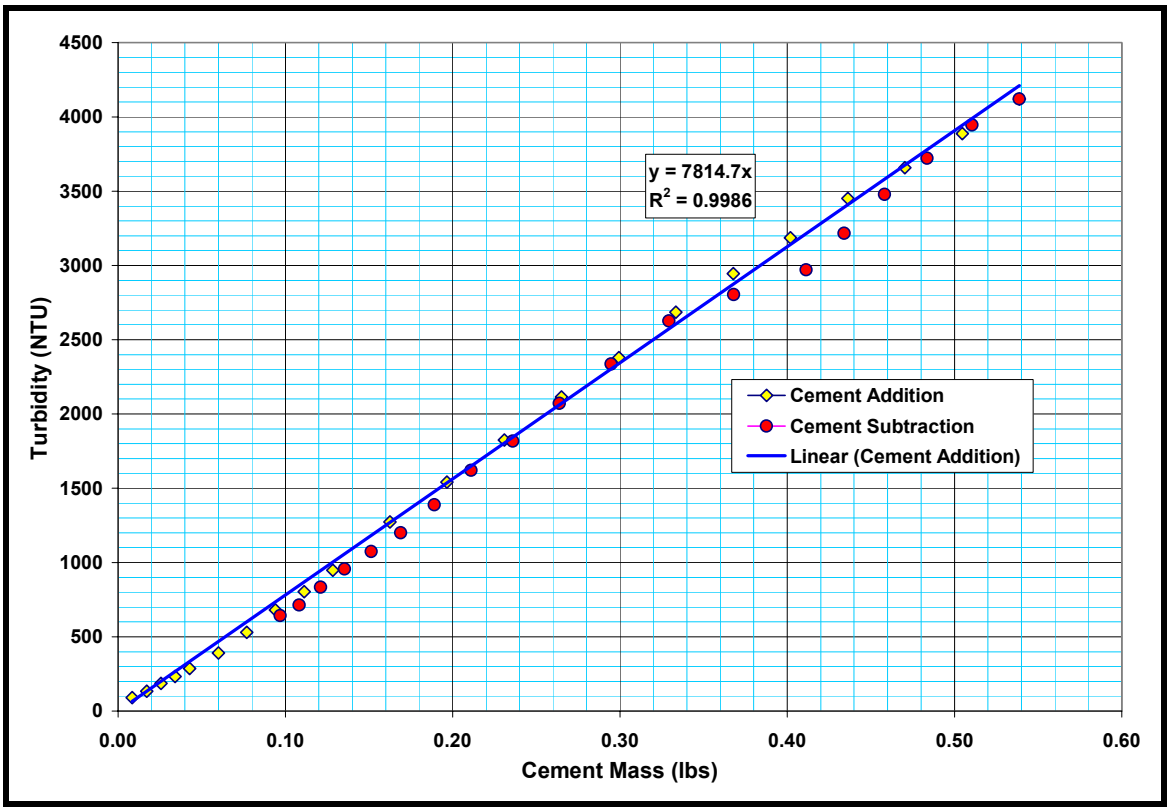

Figure 27 – Regression Line Relating Cement Mass to Turbidity

5. A MODIFIED & EXPANDED MICROWAVE-OVEN-DRYING METHOD

Although the *Specific Gravity* method had returned better results than any existing method for quantifying *W/CM*, the investigators recognized a potential limitation in that Equation 3 requires up to four mass measurements for each specific gravity measurement (as demonstrated by Equation 5). While pondering this limitation, the investigators recognized that a simplified water-to-cementitious-materials equation could be written as the water-to-solids ratio of a sample divided by the cement-to-solids ratio of the sample. The resulting equation is as follows:

$$\frac{W_{water} / W_{solids}}{W_{cement} / W_{solids}} = \frac{W_{water}}{W_{cement}} = W / CM \qquad \text{Equation (6)}$$

As shown by Equation 6 above, the water-to-cementitious-materials ratio (*W/CM*) can be determined without bias and without assumption if the following two parameters can be accurately and precisely known (or measured):

- Water-to-solids ratio (W_{water} / W_{solids})
- Cementitious-materials-to-solids ratio (W_{cement} / W_{solids})

In an effort to evaluate the potential advantages of this "simplified" *W/CM* equation, the investigators developed a procedure that is an adaptation and extension of AASHTO T 318-02, *Standard Method of Test for Water Content of Freshly Mixed Concrete Using Microwave Oven Drying* wherein a microwave oven is used to measure the water-to-solids ratio of a mortar sample and a "filter bag" is used to measure the cementitious-to-solids ratio of the sample.

5.1 Modifications

After re-considering the research from previous studies, the investigators hypothesized that the existing *Microwave-Oven-Drying* method could be greatly improved by applying two different screening/filtration processes:

1. By eliminating the coarse aggregate from the sample (thus leaving a "mortar-only" specimen), the errors associated with Difficulties 2, 4, and 5 would be reduced (see Section 2.4). If done correctly, this modified microwave-oven method could be a robust way to measure the water-to-solids ratio as shown in Equation 6. The investigators were able to implement the same coarse aggregate screening process used in the *Paste Extraction* method (see Section 4).
2. In order to accomplish a suitable means for measuring the cementitious-materials-to-solids ratio (*CM/S*), the investigators developed a procedure wherein, after the screened specimen has been completely dried by the microwave oven, a 55-micron filter bag is used to separate the dry cementitious materials from the remaining dry solids, thus allowing a reasonable determination of *CM/S*.

5.2 Testing and Results

The investigators hypothesized that sieving out the coarse aggregates would greatly reduce the error in the *Microwave-Oven-Drying* method, particularly the error associated with the moisture absorbed by the aggregates. In addition, the investigators were optimistic that the filter bag could be an effective tool to separate the cementitious materials from the remaining dry solids, which, in this case, was mostly fine aggregate. The ensuing evaluation showed exceptional results.

The regression line in Figure 28 demonstrates very good predictive capability of *W/CM* using the investigators' *Microwave-Oven / Filter-Bag* method, with a coefficient of determination (R^2) of 98.7% and a standard error of 2.2%. This standard error implies that for a measured *W/CM* equal to 0.50, the true *W/CM* can be expected to fall within the range of 0.48 and 0.52 (with 95% confidence).

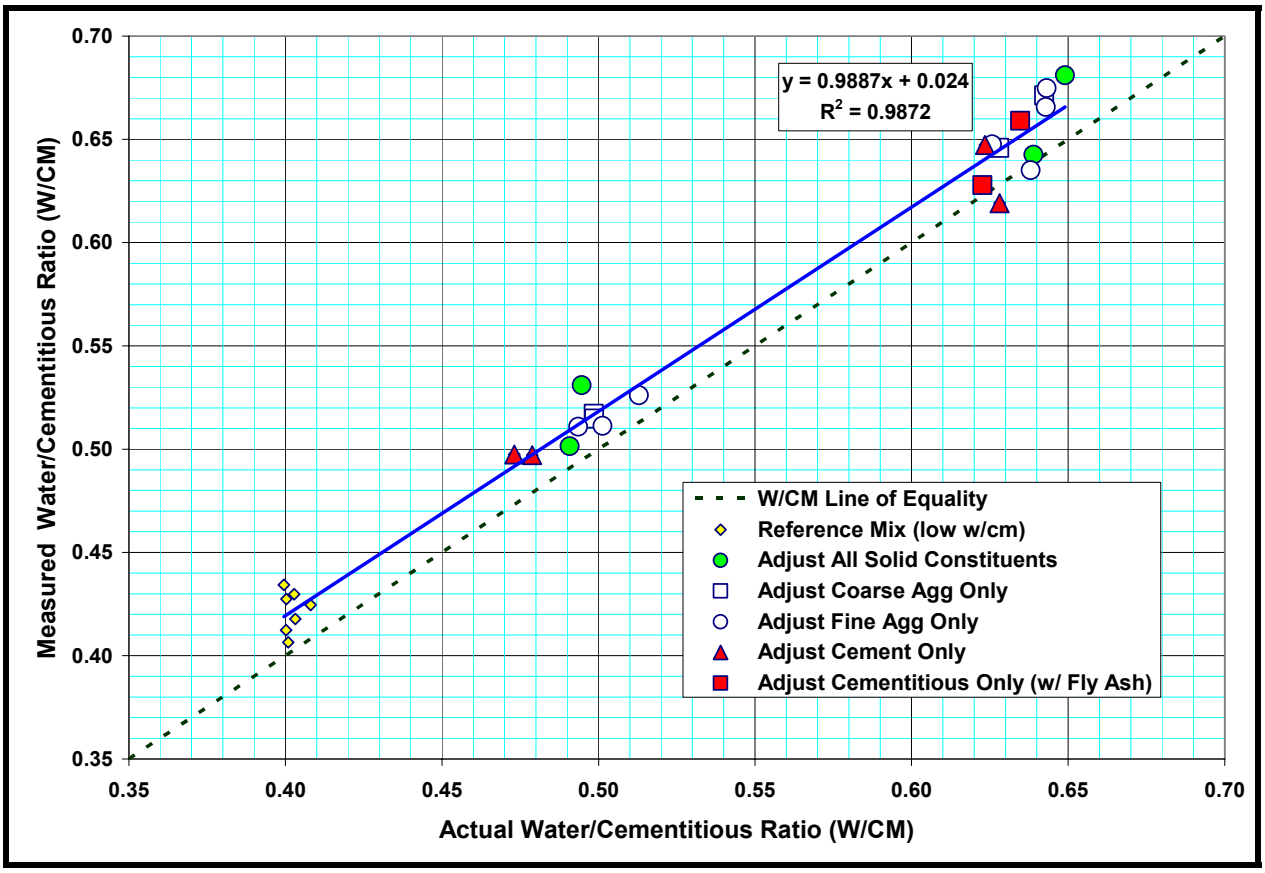

Figure 28 – Comparison of Calculated to Measured Water/Cementitious Ratio (using Microwave Oven and Filter Bag)

6. CONCLUSIONS & RECOMMENDATIONS

Table 1 below shows the comparison of standard error values for three of the *W/CM* measurement methods evaluated. As can be seen, the modified *Microwave-Oven-Drying with Filter-Bag* method yielded the most promising results.

Table 1: Comparison of Standard Error for Different Methods of Quantifying *W/CM*

Methods for Quantifying *W/CM* (Sample *W/CM* = 0.50)			
	Conventional Microwave Oven-Drying	**Specific Gravity & Turbidity**	**Modified Microwave Oven-Drying / Filter Bag**
Standard Error	**10.0%**	**6.9%**	**2.2%**
Lower Bound (95% C.I.)	**0.40**	**0.43**	**0.48**
Upper Bound (95% C.I.)	**0.60**	**0.57**	**0.52**

Based on the observations made and results obtained through this research, the investigators recommend the following future research:

- Perform additional testing and validation of the most promising methods:
    - Use a greater variation of concrete mixes and supplemental cementitious materials.
    - Evaluate the effect of cement coarseness on the measured results.
    - Place more emphasis on the variation in the water content of the aggregates.
    - Evaluate the use of a non-reactive "washing solution" to aid with the extraction step for low *W/CM* mixes in regards to the *Paste Extraction and Turbidity* method. The added fluid could be accounted for in the regression of the turbidity data.
    - Evaluate the use of alcohol instead of water to wash samples to facilitate more effective air removal.
    - Concerning the *Microwave-Oven-Drying / Filter Bag* method, repeat the experiments using larger samples, variations in coarse and fine aggregates, variations in cement fineness, variations in supplemental cementitious materials, etc.
- Develop equipment for the *Microwave-Oven-Drying / Filter Bag* method to automate the following steps:
    - Remove the coarse aggregate from the concrete specimen.

- Weigh the remaining mortar specimen.
- Dry the mortar specimen.
- Weigh the dry mortar specimen.
- Remove the cementitious materials (e.g. using forced air flow through a 55-micron filter bag).
- Weigh the remaining fine aggregate specimen.
- Calculate the *W/S*, *S/CM*, and thus the *W/CM* from the automated measurements.

7. REFERENCES

Dowell, A. and S. Cramer (2002). *Field Measurement of Water-Cement Ratio for Portland Cement Concrete - Phase II: Field Evaluation and Development*, WHRP Report 02-002, Wisconsin Highway Research Program, Madison, WI.

Halstead, W. J. (1993). *NCHRP Synthesis of Highway Practice 187: Rapid Test Methods for Asphalt Concrete and Portland Cement Concrete*, Transportation Research Board, National Research Council, Washington, D.C.

Hossain, M., Koelliker, J., Ibrahim, H. and Wojakowski, J. (1996). *Kansas Water-Cement Ratio Meter: Preliminary Results*, Transportation Research Record No. 1532, Transportation Research Board, National Research Council, Washington, D.C., pp.73-79.

Nagi, M. and D. Whiting. (1994). "Determination of Water Content of Fresh Concrete Using a Microwave Oven." *Cement, Concrete and Aggregates.* CCAGPD, Vol. 16, No. 2: 125-131.

Tom, J. G. and A. D. Magoun. (1986). *NCHRP Report 284: Evaluation of Procedures used to Measure Cement and Water Content in Fresh Concrete.* Transportation Research Board, National Research Council, Washington, D.C.

APPENDIX A: DATA FROM TURBIDITY EVALUATION

Type of Material	Total Mass (lbs.)	Turbidity Reading (NTU)
Cement	0.000	0
Cement	0.003	89
Cement	0.005	182
Cement	0.008	219
Cement	0.010	446
Cement	0.013	524
Cement	0.015	760
Cement	0.050	1000
Cement	0.105	522
Cement	0.158	179
Cement	0.206	66
Cement	0.264	27
Cement	0.317	20
Cement	0.421	16
Cement	0.475	10
Cement	0.525	8
Sand	0.000	0
Sand	0.080	7
Sand	0.160	14
Sand	0.240	21
Sand	0.320	28
Sand	0.400	35
Sand	0.480	42
Sand	0.560	49
Water	0.000	395
Water	0.110	387
Water	0.220	379
Water	0.330	371
Water	0.440	363
Water	0.550	355

APPENDIX B: DATA FROM SPECIFIC GRAVITY EXPERIMENTS

Type of Adjustment	Calculated Specific Gravity	Measured Specific Gravity	Calculated W/CM	Measured W/CM
Reference Mix (low w/cm)	2.548	2.596	0.331	0.254
Reference Mix (low w/cm)	2.548	2.562	0.331	0.306
Reference Mix (low w/cm)	2.548	2.568	0.331	0.298
Reference Mix (low w/cm)	2.548	2.538	0.331	0.345
Reference Mix (low w/cm)	2.548	2.548	0.331	0.330
Fine Agg Only	2.519	2.524	0.429	0.367
Fine Agg Only	2.519	2.534	0.429	0.351
Fine Agg Only	2.519	2.499	0.428	0.409
Fine Agg Only	2.434	2.433	0.571	0.524
Fine Agg Only	2.434	2.453	0.572	0.488
Fine Agg Only	2.434	2.422	0.568	0.542
Coarse Agg Only	2.347	2.360	0.669	0.637
Coarse Agg Only	2.347	2.358	0.669	0.641
All Solid Constituents	2.333	2.356	0.671	0.688
All Solid Constituents	2.333	2.363	0.671	0.673
Cement Only	1.643	1.646	0.745	0.739
Cement Only	1.643	1.655	0.745	0.725
Cement Only	1.426	1.452	1.284	1.193
Cement Only	1.426	1.456	1.284	1.181
Cement Only	1.426	1.441	1.284	1.231

APPENDIX C: DATA FROM MICROWAVE-OVEN-DRYING / FILTER BAG EXPERIMENTS

Type of Adjustment	Calculated W/CM	Measured W/CM
Reference Mix (low w/cm)	0.400	0.434
Reference Mix (low w/cm)	0.400	0.412
Reference Mix (low w/cm)	0.400	0.427
Reference Mix (low w/cm)	0.401	0.406
Reference Mix (low w/cm)	0.403	0.430
Reference Mix (low w/cm)	0.403	0.418
Reference Mix (low w/cm)	0.408	0.425
All Solid Constituents	0.491	0.501
All Solid Constituents	0.495	0.531
Coarse Agg Only	0.498	0.517
Coarse Agg Only	0.499	0.515
Fine Agg Only	0.494	0.511
Fine Agg Only	0.501	0.511
Fine Agg Only	0.513	0.526
Cement Only	0.473	0.497
Cement Only	0.479	0.497
All Solid Constituents	0.639	0.643
All Solid Constituents	0.649	0.681
Coarse Agg Only	0.628	0.646
Coarse Agg Only	0.642	0.671
Fine Agg Only	0.626	0.648
Fine Agg Only	0.638	0.635
Fine Agg Only	0.643	0.666
Fine Agg Only	0.643	0.675
Cement Only	0.623	0.647
Cement Only	0.628	0.619
Cement Only	0.686	0.718
Cementitious Only (w/ Fly Ash)	0.623	0.628
Cementitious Only (w/ Fly Ash)	0.635	0.659