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A Concrete Strength Model to Optimize Concrete Mixtures

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Testing for some elements of this project took place at the National Ready Mixed Concrete Association’s Testing Laboratory in College Park, MD

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A CONCRETE STRENGTH MODEL TO OPTIMIZE CONCRETE MIXTURES

By Edwin R. Dunstan Jr.
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INTRODUCTION

The author has spent more than 49 years researching concrete materials. Considering the deficiency of reliable models for concrete strength, the author has made many attempts over the years to develop a model. The model outlined in this report includes coefficients (factors) for each concrete making material. It is recognized that there are still many unknowns and no model (equation) can cover everything. However, this model is a major step forward and the primary goal is reliable predictions for 28-day strengths of concrete. The basic observation is if the initial mixture – strength correlations are well established, the model is accurate in predicting strength at early ages, 1-day, 3-days, 7-days and 28-days; with less accuracy for later-age strength at 90 days and 1 year.

Several researchers have produced equations to predict concrete strength. Some of the most referenced equations are those of Feret[1] in 1892, Abrams[2] in 1918, and Bolomey[3] in 1926. Powers and Brownyard in a continuing series entitled *Studies of the Physical Properties of Hardened Cement Pastes* was published in the *Journal of the American Concrete Institute* between October 1946 to April 1947. The author has used throughout this paper a summary of those papers written by Powers[4] and published by the Portland Cement Association in July 1958.

In the 1980s, the author was involved in the design of an Electric Power Research Institute (EPRI) funded research project to model concrete properties. The following is a quote from the first report Baker/TSA, Inc in 1987[5]:

> *Based on previous research, Dunstan developed relationships for estimating the compressive strength of cured concrete from a fly ash "lime affinity" factor and "equivalent cement" parameters. The resulting predictive equations are extensive modification of Feret's equation for concrete strength and include considerations of fly ash content, the available lime released by cements, maturity of the lime-fly ash reactions and the cementitious characteristics of fly ashes.*

The author encountered various problems with the Feret model and additional modelling work (equation development) by the author was funded by EPRI in 1989[6] as a follow-up to the Baker/TSA, Inc. study. In the follow up study, the author used the Model of Powers[4]. The author has used the reasoning of Powers in various forms over the years and this report includes major modifications of the Powers' model. It is demonstrated that the Powers' model includes factors that can be modified to address air content, the effect of chemical admixtures, and supplementary cementitious materials such as Class C and F fly ash, slag cement, silica fume, metakaolin, and other pozzolans.

The author uses concrete compressive strength data from the 1989[6] report to confirm and calibrate the model or identify problems with the data. The 1989[6] report includes concrete mixtures from five different laboratories (referenced later in this report as Regions 1 to 5).

1. Each laboratory produced five control mixtures with no fly ash and 12 concrete mixtures with two fly ash percentages for a total of 85 concrete mixes without air entrainment and water reducing admixtures.
2. Each laboratory produced two control mixes with a water reducing admixture, no air entrainment and 10 concrete mixtures with a water reducer and three different fly ashes at two different percentages for a total of 60 concrete mixtures.
3. Each laboratory produced two control mixtures with air entrainment and water reducing admixture and five test mixtures with one percentage of fly ash for a total of 35 concrete mixtures.

4. The number of concrete mixtures in (1) through (3) were target numbers. There was some variation by region, the total number of concrete mixtures was approximately 180. There were also five additional mixtures with 50-60% fly ash. Not all laboratories (Regions) produced concrete mixtures with 50-60% fly ash. This brings the total number of concrete mixtures to approximately 185.

In the early 80s, the author conducted a research project for the U.S. Bureau of Reclamation (USBR), Denver, Colorado. The mix designs for the project were those proposed by the author and he assisted with the production of concrete mixtures at the USBR. All the compressive strength test results from this research are included in a report in 1995 by von Fay[7]. At the time the mixtures were made, the author submitted his first strength model to the USBR after obtaining the 28-day strength results. This model predated the 1987[5] and 1989[6] models and was a poor model that was not based on any of the models discussed earlier in this report. However, subsequent durability papers were written by others, one on freeze-thaw durabilty[8] and another on sulfate resistance[9]. The concrete compressive strength data from the von Fay report will also be used to calibrate and confirm the model described in this report.

The von Fay report includes concrete strength data (air entrained, no chemical admixtures) and includes five control mixtures with no-fly ash. This report also includes 30 concrete mixtures with three different fly ashes with varying CaO content. Five concrete mixtures were made with each fly ash at two different total cementitious materials content and the fly ash percentages varied from 10% to 100% replacement. The total number of concrete mixtures is 35.

The author also incudes in this report early research by the USBR on the use of chemical admixtures in concrete[10]. This report includes 50 concrete mixtures with and without a chemical admixture (a 40% solid lignin chemical admixture used at 4 different dosages). Ten of the concrete mixtures where made and cured at concrete temperatures which were lower and higher than standard lab-cured concretes. This report was written by Elwood L. Ore in 1981.

The Ore report[10] will be the first concrete data used to develop the model for concrete strength using cement only. The USBR used very meticulous concrete trial batch procedures to produce high quality strength results. This author used the same procedures in his research on fly ashes beginning in 1973 (36 mixes) and published in 1984[11]. These procedures were also used for the research in the von Fay[7] report. The Ore[10] data was chosen for the preliminary model because of the known laboratory procedures, but this author was not involved in that work. The Ore[10] report includes compressive strength data for duplicate mixtures at several w/c ratios. The strength data for duplicate w/c ratios was essential in the development of the model.

As part of this research report, the National Ready Mixed Concrete Association (NRMCA) Laboratory in College Park, Maryland, with input from the author, produced 27 concrete mixtures that were used to confirm the model in this report and to demonstrate that the calibrated model for that set of materials can accurately predict concrete strengths.

A phase II of this research could be considered whereby the concrete strength model can be used to estimate some durability properties of concrete. Freeze-thaw resistance and sulfate resistance was evaluated in the EPRI funded research and in the USBR research by von Fay. If a Phase II of this research is supported, the durability data can be compared to the concrete strengths and secondary material coefficients to predict durability. The author has demonstrated the relationship for sulfate resistance[12].

This report will conclude by demonstrating how concrete producers can use the model to optimize their concrete mixtures. This report includes an Excel spreadsheet that performs the necessary model calculations to calibrate it for the specific materials and use it for predictions. This spreadsheet permits the user to calibrate the model and to select the strength level for a suggested mix design. For a specified strength, the user can choose a strength overdesign level to request mixture proportions. For example, for a specified strength of 4000 psi, the user may choose an overdesign of 1000 psi, a target strength of 5000 psi and the Excel spreadsheet will output the mix design for that strength. It is recommended that this be validated by a lab trial batch.

HYDRATION IS THE "KEY"

The author used Feret equation with modifications for the initial development of the model. However, the Feret model, as well as the Abrams and Bolomey models, do not include maturity that accounts for the increase in strength due to the hydration of cement and supplementary cementitious materials in a concrete mixture. These models also assume that the degree of hydration of cement at 28-days is the same for all water to cement ratios. For example, for a mixture with 242 lbs. of water and 500 lbs. of cement; w/c ratio 0.48, while a mixture with 242 lbs. of water and 600 lbs. of cement has a w/c ratio of 0.40. Is the degree of hydration of cement in these two mixtures the same? Most papers in the literature assume 100% hydration for both w/c ratios. The equations use the total cement quantity and the compressive strength at a constant age (for example 28-days) to develop coefficients that can be used to predict strength at 28-days. However, in this illustration, the degree of hydration of 500 lbs. of cement in one mixture is different than the degree of hydration 600 lbs. of cement because the w/c ratios are not the same. The relationship between w/c ratio and hydration is the "key" used by the author to produce a workable model (equation) for concrete strength. This "key" can also explain how admixtures influence the hydration of cement. The "key" explains (1) how water reducing admixtures increase strength, (2) how filler effect (nucleation) increases the amount of cement hydration and (3) it is also used to explain how changes in temperature effect concrete strength.

The early model based on Feret worked reasonably well but lacked the ability to effectively describe all the materials used to make concrete[5]. The primary issue was that the Feret equation could not be easily modified to include the hydration of cement and fly ash and the corresponding changes in hydration due to admixtures. In the follow-up study[6] with the same data, the author used the Powers[4] model.

THE POWERS' MODEL

The Powers' model includes a hydration coefficient for cement that varies from 0 for unhydrated cement to 1 for complete hydration. The Powers' model[4] equation is shown below:

$$S = A\,(X)^{B} \qquad \text{Eqn. 1}$$

Where:

S = compressive strength of concrete
A & B are coefficients for a set of materials
X = Gel-space Ratio

Note: From mortars, Powers[4] suggested the following equation $S = 34{,}000\ X^3$
The Gel-space Ratio is determined in equation No. 2 below:

$$X = \frac{2.06\ H_C C_V}{(H_C C_V + W_V)} \qquad \text{Eqn. 2}$$

Where:

H_C = degree of hydration of cement at a specified age (0 to 1)
2.06 = a volume constant suggested by Powers
C_V = Volume of cement per cubic yard
W_V = Volume of water per cubic yard

There are many published papers using the Powers equation for strength; however, all these papers knowingly or unknowingly assume a degree of hydration H_C = 75% (0.75) or 100% (1.00) or some number between 0 and 1 regardless of w/c ratio. In Table 1, the author calculates the constants A and B for the Powers model assuming 100% (1.0) hydration for the 28-day strength test results from the Ore[10] report. The constants are calculated from a linear regression equation Y = Slope * X + Intercept with equation No. 1 reformulated as equation No.3 below:

$$\mathrm{Ln}(S) = B \times \mathrm{Ln}(X) + \mathrm{Ln}(A) \qquad \text{Eqn. 3}$$

Table 1—Predicted Strength Using Linear Regression

Data from Ore[10] - USBR
28-Day Strength; Target Slump 3.0 in.; Target air content 5.0%
Assumed H_C = 100% all w/c ratios

Water, lb	Cement, lb	w/c	Measured Strength, psi	Predicted strength, psi	Air content, %
273	775	0.35	6950	6837	5.5
246	547	0.45	5310	4911	4.9
235	522	0.45	4600	4903	4.4
234	469	0.50	4140	4201	5.1
234	468	0.50	3900	4187	5.0
248	451	0.55	3870	3599	4.0
240	435	0.55	3490	3578	4.5
242	372	0.65	2720	2700	5.2

A = 31965; B=3.579
Average Measured Strength = 4373 psi
Average Prediction Error = 193 psi (4.42%)

Ore[10] used the Abrams[2] model to predict strength for these same data which produced an average prediction error of 251 psi. The Powers[4] model appears to be better for these concrete mixtures with a lower prediction error of 193 psi.

A review of the data shown in Table 1 points to the following four questions about the prediction error of 4.42% and whether it can be improved. These questions are discussed in more detail.

1. How good are these data? Is there an error associated with testing?
2. Why does the same w/c ratio produce different strengths? For example, the two mixtures with a w/c ratio of 0.45 have significantly different measured strengths of 5310 and 4600 psi and the two mixtures with a w/c ratio of 0.55 had measured strength of 3870 and 3490 psi.
3. The cement in each concrete mixture was assumed to have 100% hydration. What is the real degree of hydration at 28 days and is it the same for each w/c ratio?
4. How does the variation in air content impact compressive strength?

QUESTION 1 - HOW GOOD ARE THESE DATA

Quality control of laboratory procedures and data collection is critical. Strength testing variation can be due to many factors as discussed in ASTM C192. The USBR Laboratory set the standards that were later captured in ASTM C192.

- Constant Temperature – At the USBR Laboratory all materials were stored indoors for a long period of time before they were used and in a constant temperature environment.
- Cement – The cement was a mixture of several cements, that were thoroughly blended with no lumps and were stored in dry sealed 55 gallons drums. A large volume of cement was prepared at one time to ensure that the same cement could be used for several mixtures and research programs.
- Aggregates – The USBR obtained a large quantity of aggregate. The aggregate was stored indoors and separated into individual size fractions for both the coarse aggregate and sand. The aggregate used in each batch contained fine and coarse aggregate that had the same grading in that each material fraction was batched separately by weight to ensure that the same combined aggregate grading was used. The

moisture condition was consistent - laboratory temperature and dry. The Bureau used a constant sand percentage method to proportion the aggregates. For each mixture and at every w/c the sand to coarse aggregate ratio by weight was constant. This allowed for better control of water content in each mixture.

- Batching and Mixing – Each size fraction of aggregates and the cement and water was weighed accurately. The mixer was buttered with a smaller mixture having the same proportions as the mixture to be tested that followed. After each trial batch the mixer was washed out and buttered with the small batch of the next mixture to be mixed. All the water was placed in the mixer and the cement, sand and coarse aggregate was added together by power lift to introduce the materials into the mixer. The mixing procedure used the same timed procedures of mixing, stopping the mixer, and then completion of mixing. The concrete was controlled by unit weight. If the slump or air was not correct adjustments were made and a second batch was weighed up and mixed. It was ensured that the measured unit weight of the mixed concrete was very close to the design unit weight.
- Cylinders – If the batch met the requirements for slump and air within set tolerances, concrete cylinders were cast. All cylinders cast were of 6 by 12-in. size. The cylinders were consolidated by vibration using a specific time to ensure the same level of vibration for all cylinders. The concrete cylinders were not moved for the first 24 hours, then stripped and placed in a large well-controlled 100% humidity environment and cured until the age tested. The cylinders were capped with sulfur mortar for testing.
- Number of Specimens – Three concrete cylinders were tested at each test age. ASTM suggests that three batches of concrete be made on different days for a test result. This was not the case for this study, some of the mixes were repeated and the results are shown for each mixture. Some of the USBR data was the average from mixtures repeated 10 times. These data in the USBR Concrete Manual are used to determine the effect of air content on strength.

In conclusion, the data from this report (Ore[10]) is very reliable to model concrete strength with cement only mixtures and to measure the effect of a historical chemical admixture. Yes, there is testing error. Even with these data, there will be prediction errors due to testing. However, testing error is minimized with this set of concrete mixtures.

QUESTION 2 - WHY DOES THE SAME W/C RATIO PRODUCE DIFFERENT STRENGTHS?

Reviewing Eqn. 1, Powers[4] relationship for cement paste strengths, and the following quote:

> *The proportionality factor, 34,000, for this cement and type of test specimen, might be considered a measure of the intrinsic strength of the gel itself, it being the strength when the gel-space ratio is unity.*

The author questions whether 34,000 psi represents an intrinsic value. Testing of cement pastes by Roy, et.al.[13] produced strengths in excess of 90,000 psi. The factor 34,000 psi is an empirical constant for the gel-space ratio developed by Powers for his specific mixtures. However, this author suggests that there is an important intrinsic value in Eqn. 1, that is the exponent 3. The exponent 3 is “intrinsic” in that compressive strength is three (3) dimensional - a “calculated hydration ratio” cubed. The author will demonstrate how a cubed relationship is used to model strength.

Reviewing the data in Table 1, the strengths for the repeated concrete mixtures for w/c ratios of 0.45 and 0.55 are compared. For each w/c ratios, the second mixture has a lower cement content and lower strength. The gel-space ratio of Powers is the same for constant w/c ratios. The gel-space ratio for both mixtures with a w/c ratio of 0.55 is approximately 0.753. The volume of hydrated cement, assuming 100% hydration, can be determined from the numerator of Eqn. 2. The first concrete mixture this value is 4.727 and for the second it is 4.559. The ratio is $(4.559 \div 4.727) = 0.964$. The ratio of the strength of these mixtures is $(3490 \div 3870) = 0.902$. The strength in the Powers equation is related to the 3rd power (Intrinsic). That is if 0.964 was raised to the third power the result is $0.964^3 = 0.895$ compared to 0.902. The strength in the Powers equation is related to the 3rd power (Intrinsic). Raising 0.964 to the third power; $0.964^3 = 0.895$ compared to 0.902. Notice that the air content is not the same. The first mixture has a lower air content of 4.0% compared to 4.5% for the second. The same calculations for the 0.45 w/c ratio mixtures gives 0.869 and 0.866. This suggests that using the hydrated volume in the numerator of Eqn. 2 (as calculated by Powers) is superior to Powers' Gel-Space Ratio to predict the strength of concrete.

Considering some volumetric issues.
Compare two mixtures with W/C ratios of 0.40 and 0.70 with a water content of 280 lb/ft^3 (4.49 ft^3).
The cement contents are 700 lb/ft^3 (3.56 ft^3) and 400 lb/ft^3 (2.04 ft^3) respectively.
The hydrated cement volume from the numerator of the gel-space ratio is 7.34 ft^{3}and 4.19 ft^3.
Expressing this as a ratio of the total volume: Mix 1 is $(7.34 \div 27) = 0.272$; and Mix 2 is $(4.19 \div 27) = 0.155$.
The relative ratio is $0.272 \div 0.155 = 1.75$.

How does this compare to the gel-space ratio in 1 cubic yard (27 ft^3)?
The gel-space ratios for these mixtures are based on Eqn. 2 with 100% hydration:
$(1 \times 2.06 \times 3.56) \div [(1 \times 3.56) + 4.49] = 0.911$; and
$(1 \times 2.06 \times 2.04) \div [(1 \times 2.04) + 4.49] = 0.643$
Expressing it relative to one cubic yard of concrete:
Mix 1 is $(0.916 \div 27) = 0.034$; and
Mix 2 is $(0.643 \div 27) = 0.024$.
The relative ratio is $(0.034 \div 0.024) = 1.42$.

Using the gel-space ratio in 27 ft^3 gives a significantly different number than comparing the amount of hydrated cement in 27 ft^3. The question is which one is correct? There have been a lot of studies that find a direct relationship between the amount of heat generated by hydration to strength. The author has used the relationship between the volume of hydrated cement $H = 2.06\, H_C\, C_V$ (which produces heat) divided by 27 in Table 2 for the parameter $(H/27)^3$.

Table 2—Predicted Strength with Ratio $(H/27)^3$

Data from Ore[10] - USBR
28-Day Strength; Target Slump 3.0 in.; Target air content 5.0%
Assumed H_C = 100% all w/c ratios

Water, lb	Cement, lb	w/c	Measured Strength, psi	Predicted strength, psi	Air content, %
273	775	0.35	6950	7037	5.5
246	547	0.45	5310	4976	4.9
235	522	0.45	4600	4699	4.4
234	469	0.50	4140	4066	5.1
234	468	0.50	3900	4053	5.0
248	451	0.55	3870	3734	4.0
240	435	0.55	3490	3620	4.5
242	372	0.65	2720	2694	5.2

Slope = 1972; Intercept = 41388
Average Measured Strength = 4373 psi
Average Prediction Error = 117 psi (2.69%)

The author has defined the hydrated volume ratio as $(H/27)^3$. The following relationships were evaluated:

1. Ln(strength) versus $(H/27)^3$; $R^2 = 0.7566$
2. Ln(strength) versus $\mathrm{Ln}(H/27)^3$; $R^2 = 0.9532$
3. Strength versus $\mathrm{Ln}(H/27)^3$, $R^2 = 0.9848$.

The best correlation was been found to be strength versus $\mathrm{Ln}(H/27)^3$ and this is the predicted strength shown in Table 2.

Considering the linear regression equation $Y = MX + B$,
where Y is predicted strength = $\mathrm{Ln}[(H/27)^3]$ and B is the intercept with values reported in Table 2.
These are not the final numbers for this set of materials. This discussion will next address cement degree of hydration at each w/c ratio and the effect of air content on strength. These factors will change the regression constants. In a later section, the slope and intercept values will be used to estimate the degree of hydration at each age - 1, 3, 7 and 28-days, etc. The 4th dimension to strength is the age and this is discussed later in the report.

QUESTION 3 - PREDICTING HYDRATION

The Gel-Space Ratio of Powers varies with the degree of hydration. Figure 1 below is taken from Powers[4]. Using Eqn. 1, the A =34,000 psi and B = 3 in Figure 1. The strength of 34,000 psi is described as the strength of the cement paste that is fully hydrated (100%) at a gel-space ratio = 1.0. Considering cement weight of 1.0 g with a water content is 0.3365 grams; the volume of cement is (1.0 ÷ 3.15) = 0.3175, where 3.15 is the specific gravity of cement; and the volume of water is 0.3365. Using Eqn. 2, a paste with a w/c of 0.3365 has a gel-space ratio of 1.0:

$$X = \frac{2.06 \times 1.0 \times 0.3175}{0.3175 + 0.3365} = 1.0$$

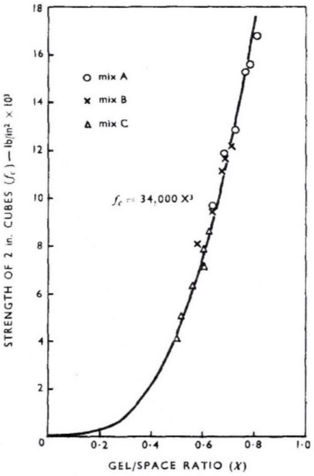


Figure 1—Gel-Space Ratio Versus Strength from Powers[4]

Powers[4] cured his pastes from 7-days to 2 years age but obviously did not achieve 100% hydration. The maximum strength data point is approximately 17,000 psi rather than 34,000 psi at 100% degree of hydration. At 17,000 psi, it indicates that the degree of hydration of cement was less than 100% even at two years. Powers and others have suggested that 100% hydration is possible for w/c ratios greater than a critical value. Is 100% hydration possible? Research by Mills[14] suggests that 100% hydration cannot be achieved using only water and cement. Mills hydrated cement pastes with high w/c ratios of 2.13 and 4.17; However, neither of these pastes achieved 100% hydration at 112 days. Is hydration somehow limited? This question is discussed in the following section.

PREDICTING H_C - CEMENT HYDRATION

Does its physical structure of cement paste limit hydration before it reaches 100%? Even after long periods of time hardened concretes can contain significant quantities of un-hydrated cement. As pointed out by Mills[14], Powers suggests that his "gel-space ratio" defines a limitation to hydration. The following is a quote from Mills[14]:

> *In his earlier work Powers suggests that in dense hydrated cement pastes hydration stops when the space originally filled with mixing water becomes filled with hydrated paste.*

In this report, it will be demonstrated that there is one physical property of a cement paste that can be used to predict the ultimate hydration of cement (H_U) - the point at which hydration ceases. This assumption is that with water alone hydration, cement paste will **not** fully hydrate even at later ages.

The ultimate degree of hydration (H_U) of cement pastes can be estimated using the hydration model of Powers with a relationship demonstrated in the following discussion.

PHYSICAL STRUCTURE OF HYDRATED CEMENT

In 1958, Powers[4] outlined the physical structure of hydrated cement in Research Department Bulletin 90 entitled *The Physical Structure and Engineering Properties of Concrete*. The following are three quotes from that publication which gives physical properties of hydrated cement paste (cement gel).

The physical properties to be given now are those of the nominal gel, which is defined as the actual gel and the calcium hydroxide associated with it.

> *The density of the nominal gel is about 2.15 g/cm^3, its porosity is about 26%...*
>
> *The gel substance proper, corrected for calcium hydroxide, has an average density of 2.65 g/cm^3.*
>
> *The hydration of one cubic centimeter of portland cement produces about 2.06 cm^3 of gel plus the non-gel constituents."*

The physical properties are illustrated in the following calculations utilizing a cement paste with 0.243 grams of water and 1.0 gram of cement. Similar calculations were made by Neville[15] using 0.23 grams of water for 1.0 gram of cement and by Mindess, et.al.[16] using 0.24 grams of water for 1.0 gram of cement. The value of 0.243 selected here will be discussed later.

Assume a paste at 0.243 w/c ratio can fully hydrate ($W_O = 0.243$, where W_O is the intrinsic number of grams of water required to hydrate 1 gram of cement). If this paste were fully hydrated the following would be true: One gram = 1÷3.15 = 0.3175 cm^3 of cement chemically combines with $W_O = 0.243$ grams of water (w/c ratio of 0.243). If the hydration of 1 cm^3 of cement produces 2.06 cm^3 of hydrated gel, then 0.3175 cm^3 of cement hydrates to a volume of (2.06 × 0.3175) =0.654 cm^3 of hydrated gel. The porosity of this gel according to Powers[4] is 26% (gel-pores). Therefore, the solid volume of the gel is [(1 - 0.26) × 0.654 cm^3] = 0.484 cm^3.

The hydration of the 1-gram of cement with a volume of 0.3175 cm^3 has increased to a volume of 0.654 cm^3.
The total original volume is 0.243 cm^3 of water plus 0.3175 cm^3 of cement = 0.561 cm^3.
The increase in volume is (0.654 ÷ 0.561) =1.167, an increase in volume of 16.7%.
The volume of the gel pores is (0.654 - 0.484) = 0.17 cm^3 = 0.17 grams = W_g (gel-water).

For w/c ratios greater than 0.243 the paste expands into water filled space and the gel-pores entrap water. This increased volume is filled with water and is termed "gel water", water internal to the gel. The remaining water that is external to the gel is called *capillary water* that fills the capillary porosity.
The total weight including gel water is 1.243 + 0.17 = 1.413 grams.
The density of this hydrated gel with water filled gel-pores is (1.413÷0.654) = 2.16 g/cm^3, which is the basically the hydrated gel density of 2.15 g/cm^3 quoted from Powers[4] and shown above.
Neville[15] using Wo = 0.23 states: *An average value of specific gravity of the products of hydration (including pores in the densest structure possible) in a saturated state is 2.16.*

A New Theoretical Approach to Hydration Limits

The data from Mills[14] indicates that cement pastes with w/c ratios between 0.25 to 4.70 cease hydration at less than 100% hydration where there is un-hydrated cement and free water in the system. The free water is in excess of that chemically bound and within the gel pores. In this report it is assumed that as cement hydrates it expands in volume and entraps water in the hydrated structure in the gel pores and in doing so also encapsulates non-hydrated cement. This cement is sealed off from water and cannot hydrate. This assumption beginning with Eqn. 4.

$V_g = H_U C_V (2.06) (0.26)$ Eqn. 4

Where:

V_g is the volume of gel-pores
H_U is the ultimate hydration at cessation
C_V is the total cement volume
2.06 is the cement to hydrated cement constant from Powers[4]
0.26 is the porosity from Powers[4]

V_g is the volume of gel pores when they are filled with water; the water entrapped in gel pores. The original w/c ratio by volume R_V is W_V/C_V (volume of water divided by volume of cement). If the water entrapped in the gel-pores is W_g, the volume of cement associated with the gel water is $(W_g \div R_V) = C_{gv}$. This is the volume of cement encapsulated in the gel that does not react and is calculated as shown in Eqn. 5 with $(V_g = W_g)$ (1 cm^3 of water = 1 gram).

$C_{gv} = V_g \div Rv$ Eqn. 5

C_{gv} is the volume of cement assumed to be entrapped in the gel and sealed off from water and will not react. This is therefore the amount of un-hydrated cement at cessation of hydration.

The un-hydrated cement can be estimated relative to the total volume of cement. If the amount of hydrated cement at cessation of hydration is $H_U C_V$, the amount of non-hydrated cement is determined by Eqn. 6.

$C_{gv} = (1 - H_U) C_V$ Eqn. 6

If the assumptions above are true, cessation of hydration will occur when Eqn. 5 equals Eqn. 6. The following relationships also apply.
The mass (weight) of water is W_W grams = volume of water of W_V cm^3.
The mass (weight) of cement $C_W = 3.15 C_V$.
Water to cement ratio by weight is $R_W = W_W \div C_W$.
Water to cement ratio by volume is $R_V = W_V \div C_V$ and $R_V = 3.15 R_W$.

Using these relationships, first substitute Eqn. 4 into Eqn. 5. Set Eqn. 5 equal to Eqn. 6 and solve for H_u. The following relationship is derived for cessation of hydration.

$H_U = R_W \div (R_W + 0.17)$ Eqn. 7

$H_U = (w/c) \div [(w/c) + 0.17]$

R_W is water to cement ratio (w/c) by weight

The calculated value "0.17" in Eqn. 7, is the same as the mass (weight) of water in gel-pores. Eqn. 7 relates gel-pore volume to hydration limits.

Assume that the cement paste has a w/c ratio by weight $R_W = 0.3365$ which is a gel-space ratio of 1 at 100% hydration in Eqn. 2.
Unit volumes are $0.3365 \div (0.3365 + 0.3175) = 0.5145$ cm^3 of water and 0.4855 cm^3 of cement

On complete hydration, 0.4855 cm^3 of cement expands to a volume of 2.06 × 0.4855 = 1.00 cm^3. Considering 26% gel porosity, the solid volume of hydrated cement is 0.74 cm^3.

CESSATION OF HYDRATION—POWERS AND MILLS

The following discussion demonstrates that hydration ceases. Considering a cement paste with a w/c ratio of 0.3365. Using Eqn. 7, ultimate hydration, H_U, is estimated to be 0.3365 ÷ (0.3365 + 0.17) = 0.6644; that is degree of hydration at later ages is approximately 66%. Eqn. 2 to determine gel-space ratio is compared for 100% degree of cement hydration in Eqn. 8 and for 66% degree of hydration in Eqn. 9.

$$X = \frac{2.06 \times 1 \times 3175}{(1 \times 0.3177 + 0.3365)} = 1.0 \qquad \text{Eqn. 8}$$

$$X = \frac{2.06 \times 0.66 \times 3175}{(0.66 \times 0.3175 + 0.3365)} = 0.794 \qquad \text{Eqn. 9}$$

Using the gel-space ratio from Eqn. 9 in Eqn. 1 the predicted strength is:

$$S = 34{,}000\ (0.794)^3 = 17{,}000 \text{ psi} \qquad \text{Eqn. 10}$$

Powers[4] cured his pastes from 7-days to 2 years. From Figure 1, the highest measured strength at the latest age was approximately 17,000 psi, similar to that predicted by Eqn. 10. Even at 2 years, these pastes did not achieve 100% degree of hydration and one can surmise based on the similar strengths that the degree of hydration of these pastes was approximately 66%, assuming a w/c of 0.3365.

Mills[14] hydrated ball-milled slurries at various w/c ratios with a different cement than Powers with a water content to completely hydrate 1 gram of cement, W_O = 0.253 and some siliceous rock flour and at a w/c of 0.35 to a measured strength of 18,000 psi at 448 days. W_O = 0.253 is greater than that suggested by Neville[15] (0.23), Mindess et al.[16] (0.24) and 0.243 suggested by this author. Each cement is unique. W_O will vary depending upon the chemistry of the cement and gypsum content. A concrete producer using this model will not know the exact value of W_O for the cement used by them. The value 0.243 chosen by this author is reasonably representative value for all cements. The value of 0.243 will be discussed later in this report.

The relationship in Eqn. 7 can be confirmed using the ultimate hydration data of Mills at 448 days. The comparison is shown in Figure 2 below. Powers correctly predicted that at lower w/c ratios hydration is restricted and that is shown for w/c less than 0.3365 in Figure 2. Eqn. 7 works well for w/c ratios of 0.3365 assuming 100% degree of hydration for a gel-space ratio of 1 and greater and correctly predicts the ultimate hydration, H_U, for the data reported by Mills[14].

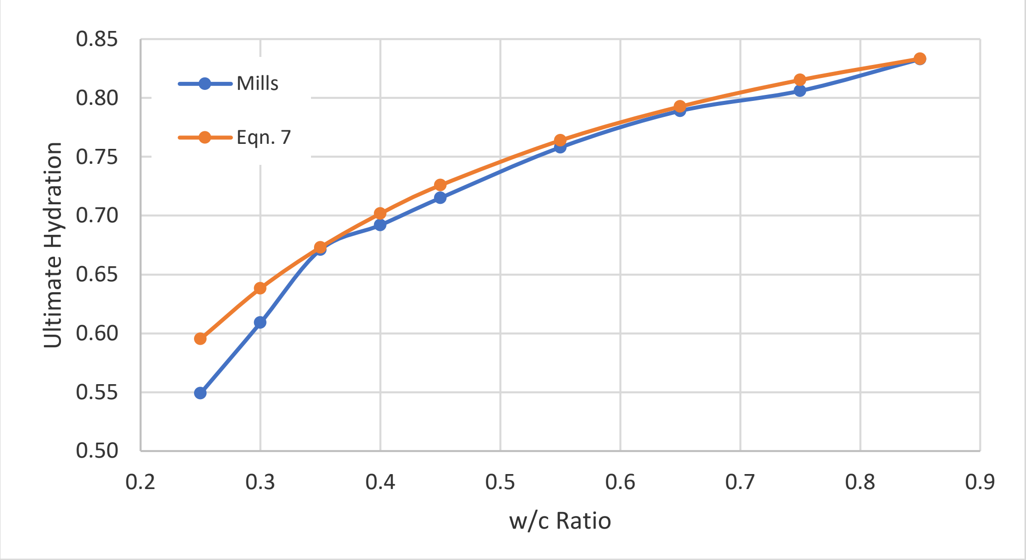


Figure 2-w/c Versus Ultimate Hydration (H_U)

Table 3 below is the same data in Tables 1 and 2, with the predicted strength using ultimate hydration based on Eqn. 7.

Table 3—Predicted Strength with Ratio $(H/27)^3$

Data from Ore[10] - USBR
28-Day Strength; Target Slump 3.0 in.; Target air content 5.0%
Ultimate Hydration H_U for all w/c ratios

Water, lb	Cement, lb	w/c (H_U)	Measured Strength, psi	Predicted strength, psi	Air content, %
273	775	0.35 (0.673)	6950	7071	5.5
246	547	0.45 (0.726)	5310	4981	4.9
235	522	0.45 (0.726)	4600	4628	4.4
234	469	0.50 (0.746)	4140	4022	5.1
234	468	0.50 (0.746)	3900	4009	5.0
248	451	0.55 (0.764)	3870	3905	4.0
240	435	0.55 (0.764)	3490	3637	4.5
242	372	0.65 (0.793)	2720	2726	5.2

Slope = 2530; Intercept = 19179

Average Measured Strength = 4373 psi

Average Prediction Error = 112 psi (2.56%)

The slope and intercept have changed from Table 2; the prediction error is reduced from 2.69% to 2.56%.

QUESTION 3 – HOW DOES AIR CONTENT EFFECT STRENGTH

Comparing Figures 1 and 3 from Powers[4] suggests how air content influences strength. Air volume is included in denominator of the gel-space ratio in Figure 3 (X_F) whereas in Figure 1 (X) above the gel-space ratio does not include air.

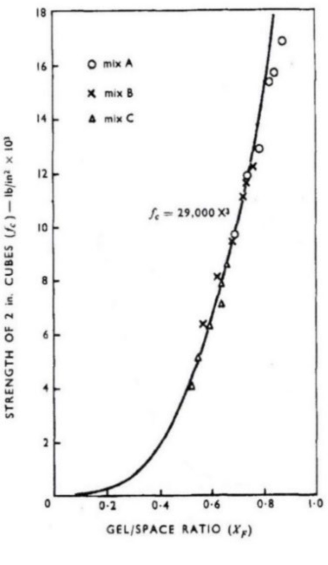


Figure 3—Modified Gel-Space Ratio with air volume included in the denominator of Eqn. 2

Strength is related to the gel-space ratio and modified ratio raised to the third power. In Figure1, A = 34,000 and in the Figure 3, A = 29,000. A cubed relationship will be used in this model and confirmed by graphs from the USBR Concrete Manual[17]. Consider the following ratio (29,000 ÷ 34,000) = 0.852; and $0.852^{1/3}$ = 0.948. Both the numerator and denominator of Powers Eqn. 2 is cubed. In Figure 3 above Powers has included the amount of entrapped air in his mortars in the denominator and his intrinsic value is reduced from 34,000 to 29,000. This is the reduction in strength due to entrapped air a cubed relationship which will be discussed below.

The industry uses rules of thumbs such as *each 1% increase in air reduces strength by about 5%.* This is possibly inferred from the USBR Concrete Manual (Figure 4 below) which suggests approximately a 20% change in strength for a change in air content from entrapped air to recommended total air content.

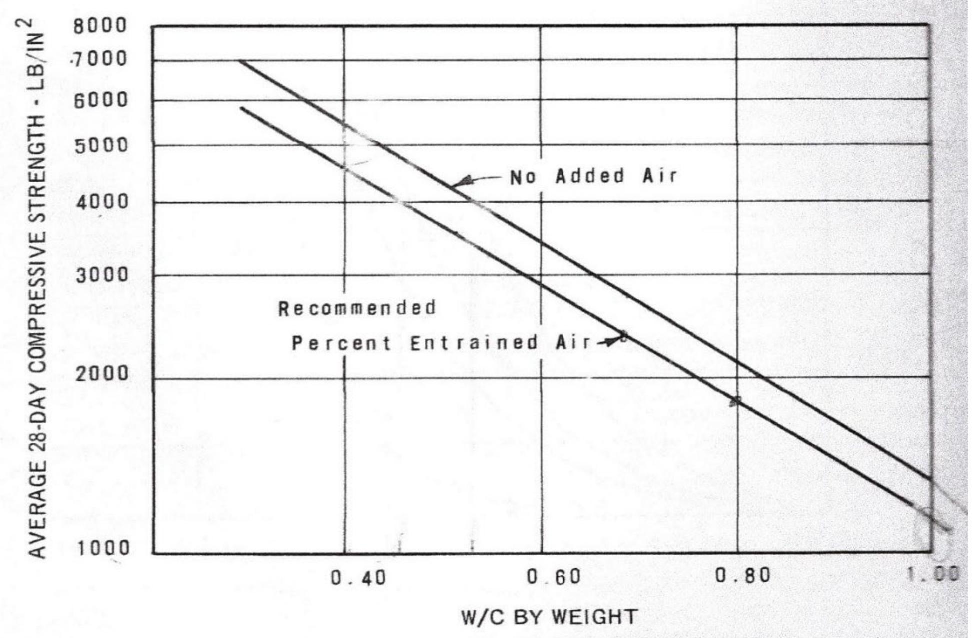


Figure 19.—Strength in relation to water-cement ratio for air-entrained and non-air-entrained concrete. Strength decreases with an increase in water-cement ratio; or with the water-cement ratio held constant, use of air entrainment decreases the strength by about 20 percent. 288–D–1524.

Figure 4—Figure 19 From USBR Concrete Manual[17]

In the above figure, the change in strength from no entrained air (entrapped) to recommended total air (entrapped and entrained) changes the strength by about 20%. The figure clarifies that there were no differences in the mixtures because the w/c ratio was held constant.

In Figure 1, Powers assumed the air content was zero, and in Figure 3 the pastes contained air. In this report, it is demonstrated that gel-space ratio needs to be replaced with $(H/27)^3$ (the hydrated volume ratio/27) defined earlier in this paper. Powers added an air component to the denominator of the gel-space ratio equation. The author suggests the following ratio to exclude air in the denominator $[H \div (27 - A_V)]^3$, where A_V is the volume of air in ft^3 in 1 cubic yard of concrete. It can be assumed if the concrete mixtures prepared by Ore[10] were air-free, the strength would be higher. What would be the increase in measured strength for air-free concrete? The author is using a cubed relationship for the prediction. Consider the first mixture in Ore data shown in Tables 1-3 which contains 5.5% air; $A_V = 1.485$ ft^3/yd^3. The measured strength was 6950 psi. The air content can be used to calculate the strength of air-free concrete (S_{NoAir}). Consider Eqn. 11 as an example shown below:

$$S_{NoAir} = \frac{\text{Measured Strength}}{(1-A)^3} = \frac{6950}{(1-0.055)^3} = 8235 \text{ psi} \qquad \text{Eqn. 11}$$

It has been shown that strength is related to the hydrated volume of cement cubed. Air is a portion of the volume and thus its effect on strength is also a cubed relationship as shown by Powers and in Eqn. 11.

Table 4 is the same data using the cubed method for air content to predict the reduction in strength for air content.

Table 4—Predicted Strength vs $(H/(27-A_V))^3$ and S_{NoAir}						
Data from Ore[10] - USBR 28-Day Strength; Target Slump 3.0 in.; Target air content 5.0%						
Water, lb	**Cement, lb**	**w/c**	**Measured Strength, psi**	**Predicted strength, psi**	**S_{NoAir}, psi**	**Air content, %**
273	775	0.35	6950	7045	8235	5.0
246	547	0.45	5310	4997	6174	4.9
235	522	0.45	4600	4669	5625	4.4
234	469	0.50	4140	4008	4844	5.1
234	468	0.50	3900	3887	4549	5.0
248	451	0.55	3870	3935	4374	4.0
240	435	0.55	3490	3640	4007	4.5
242	372	0.65	2720	2710	3193	5.2
For S_{NoAir}: Slope = 3005; Intercept = 22.218 Based on S_{NoAir} Strength Average Measured Strength = 4373 psi Average Prediction Error = 119 psi (2.71%)						

The regression constants in Table 4 differ from those in Table 3. With a coefficient of determination, $R^2 = 0.987$, the relationship is good but the prediction error had a modest increase. This relationship includes a consideration of air content of the mixtures. It is suggested that a single incorrect measured air content effects the relationship and thereby the prediction error. It is suspected that the second mixture with a measured strength of 5310 psi may have a lower air content than the reported 4.9 because of the largest predicted difference of 313 psi. If the measured air content was 4.4% rather than 4.9%, the prediction error reduces to 2.55%. Testing error, due to batching and testing procedures will impact the prediction accuracy. It is felt that the model is good for mixtures that contain portland cement only. As additional materials are used for concrete mixtures, the potential for testing and batching errors increases, thereby potentially increasing the prediction error.

The question is whether the cubed relationship for air content is appropriate as used for the predictions in Table 4. Table 5 includes changes in mixture proportions and air content changes. The first adjustment is to increase the air content by 4.0%. This increase in air decreases the water content for target slump. ACI 211 suggests a decrease in water content of 5 lbs. for each 1% increase in air and a corresponding decrease in cement content to maintain the same w/c ratio. The decrease in water content for a 4.0% increase in air is shown in Table 5. This results in 20 lb. less water and the cement weight is adjusted to a lower value for the same w/c ratio.

Table 5— (H/(27-A_V) vs. Strength – Increase Air by 4.0%l; Adjust Water						
Data from Ore[10] - USBR 28-Day Strength; Target Slump 3.0 in.; Target air content 5.0%						
Water, lb	**Cement, lb**	**w/c**	**Measured Strength, psi**	**Predicted strength (+4% air), psi**	**S_{NoAir}, psi**	**Strength ratio, %**
253	718	0.35	6950	5969	8235	86
226	503	0.45	5310	4108	6174	77
215	478	0.45	4600	3787	5625	82
214	429	0.50	4140	3209	4844	78
214	428	0.50	3900	3201	4549	82
228	415	0.55	3870	3172	4374	82
220	399	0.55	3490	2894	4007	83
222	341	0.65	2720	2075	3193	76
Strength ratio = (Predicted + 4% air) ÷ Measured Strength; Average Ratio = 81% For S_{NoAir}: Slope = 3005; Intercept = 22.218; R^2 = 0.987						

The USBR Concrete Manual suggests a reduction in strength of approximately 20% for entrained air (Figure 4). The rule of thumb the industry uses is 5% change in strength with 1% change in air content. Increasing the air content by 4.0% and adjusting cement and water accordingly, results in an average strength reduction of 19% in Table 5, which is close to the 20% approximation in the Concrete Manual. For each mixture, the strength reduction varies from 14% to 24%. It is difficult to define the exact strength loss due to the increase in air for mixtures with varying cement content.

The cubed relationship for a 4.0% air content change: $[(1 - 0.040)^3 = 0.885]$ predicts a reduction in strength of 11.5%. Relative to 20%, this accounts for approximately 60% of the strength reduction; therefore based on Table 5 it is surmised that about 40% of the strength reduction is due to changes in mixture proportions resulting in less cement for hydration. Considering the effect of air alone, in this case is (11.5 ÷ 4 = 2.9%) or approximately a 3% reduction in strength for a 1% increase in air content.

MODELLING CONCRETE MATURITY AT DIFFERENT AGES

In Table 4, the predicted strength at an age of 28-days is compared to expected strength at ultimate hydration, H_U based on Eqn. 7. Ultimate hydration occurs at later ages. In Mills[14] ball milled slurries the latest age was 448 days. Powers[4] cured his mortars for two years. It can be assumed that hydration at 28-days is significantly less than ultimate hydration and at earlier ages less than that at 28-days. This section discusses how the model is modified to calculate the hydration for each tested age.

Using the same calculations as in Table 4 regression lines for strengths at each age produce regression constants that follow a pattern. The slope and intercept of these relationships increase from 1-day to 365-days. These regression constants are used to estimate the hydration at each age.

In Table 6 are the updated regression constants for the Ore[10] test results calculated from S_{NoAir} based on Eqn. 11.

Table 6—Regression constants for Strengths vs Ultimate Hydration at various ages for Ore data[10]			
Age, Days	**Slope**	**Intercept**	**Coefficient of Determination, R^2**
1	1085	7297	0.983
3	1917	13083	0.990
7	2624	18114	0.982
28	3005	22218	0.987
90	3042	23451	0.972
365	3436	26166	0.954

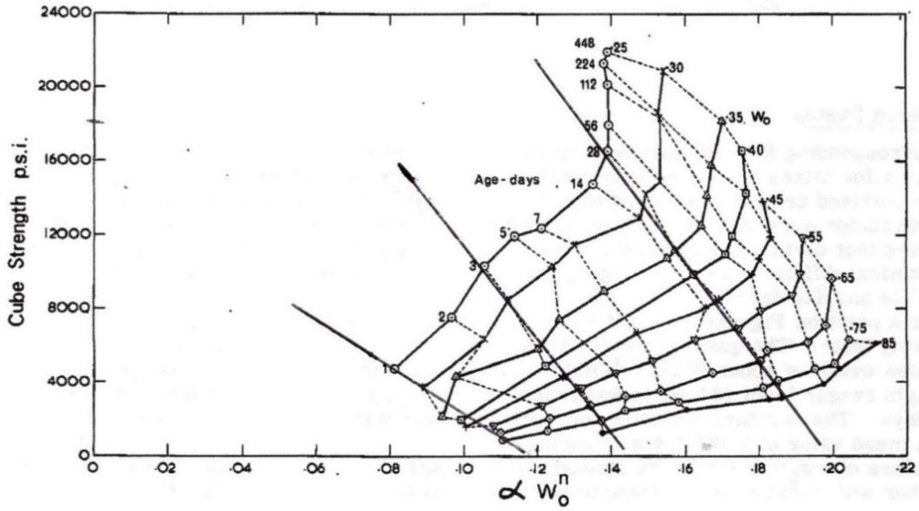


Figure 1. Observed values of cube strength and nonevaporable water for various ages and water/cement ratios for portland cement OP1.

Figure 5--- Figure 1 Modified from Mills[14]—Hydration Versus Cube Strength

Figure 5 plots the degree of hydration measured by the non-evaporable water content and strength and is taken from Mills. Straight lines are added through the data at ages of 1, 3, and 28-days. These lines indicate the slope increases with strength age and matches the trend of slopes for the Ore[10] data in Table 6 above. The change in slope is greatest between 1-day and 28-days.

At early ages 1-day to 28-days, the hydration progresses at a steady rate and slows down around 56-days. For ages greater than 56-days while there is an increase in strength, the change in hydration is small. In Table 6, the model fit, as represented by R^2 values for ages of 90- and 365-days age strengths are slightly reduced. It is expected that the strength model proposed here based on hydration are expected to have greater prediction errors for strength at ages later than 28-days.

Mills[14] stated that the strength increases with reduced hydration may *be explained in terms of a metamorphosis of the colloidal hydrate to microcrystalline material.* In this report, the focus will be on the accuracy of the hydration-based model for strengths at 28-days age and earlier. The primary focus will be the accuracy of prediction for strength at 28-days.

ESTIMATING HYDRATION FOR EACH TEST AGE

The degree of hydration in Figure 5, was determined by placing cement and water at different w/c ratios into a bottle which was sealed and contained marbles and the bottle was rotated, milled by the marbles, for the full period of time until test age – at which point cube strength and degree of hydration were determined.

In Figure 6, the degree of hydration with age is illustrated for the test samples from Mills[14]. Mills assumed that the mass of water to fully hydrate 1 gram of cement was 0.253. The degree of hydration at 28-days for a w/c ratio of 0.3365 (Gel-space Ratio=1) can be estimated from the figure. The degree of hydration at 28 days at a Gel-space Ratio of 1 is approximately 0.60. (w/c = 0.3362 at 28-days). The ultimate hydration calculated earlier is 0.66. At an age of 28-days the degree of hydration is approximately (0.60 ÷ 0.66 = 90%. This value of 90% was used in a recent paper [12], while a value of 91.4% was used in an earlier paper [18].

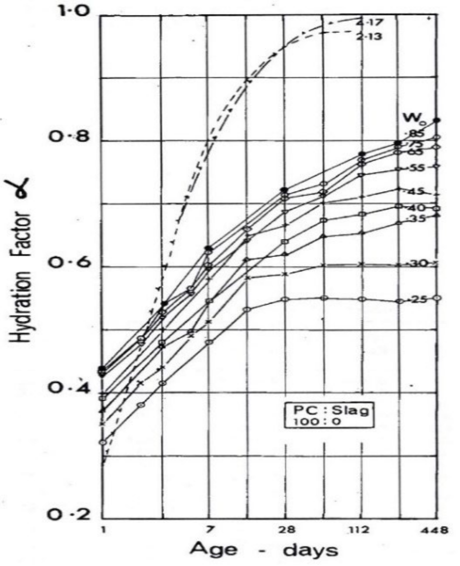


Figure 4. Variation of hydration factor α with age for portland cement pastes having various values of water/cement ratio.

Figure 6—Hydration of Portland Cement Pastes-Variation with Age and w/c Ratio

This model chooses an ultimate age for complete hydration of cement in concrete that is continually moist cured of 3814 days, or approximately 10 years. The ultimate age for cessation of hydration in concrete in reality is unknown. The USBR has tested compressive strength with age for concrete in dams[19,20]. Cores extracted from these dams indicate that concrete strength continues increasing up to 10 years, however, there is no clear indication that hydration continues or that there is any significant increase in compressive strength beyond 10 years[21]. Eqn. 12 was developed to model age in days. At ultimate hydration age, the degree of hydration is 100% of that predicted from Eqn. 7 using a value of 1 (100%) as shown below. The number of days of 3814 was chosen to result in a value of 1 as shown below.

$$\text{Age Conversion} = \mathrm{Ln}(\mathrm{Ln}(\mathrm{Ln}(\text{Age} \times 1000))) \qquad \text{Eqn. 12}$$

Age = 3814 Days (assumed ultimate age for strength gain)

$$\text{Age Conversion} = \mathrm{Ln}(\mathrm{Ln}(\mathrm{Ln}(3814 \times 1000))) = 1.0$$

In the following discussion it will be demonstrated that Eqn. 12 is directly related (with high correlation) to slope and intercept at various ages.

Review the values in Table 7:

Table 7—Factor to estimate hydration at each age	
Age, Days	**Age Conversion (Eqn. 12)**
1	0.659
3	0.733
7	0.780
28	0.844
90	0.890
365	0.936
3814	1.000

Figure 7 below is a plot of the age conversion values (Table 7) versus intercept values (Table 6).

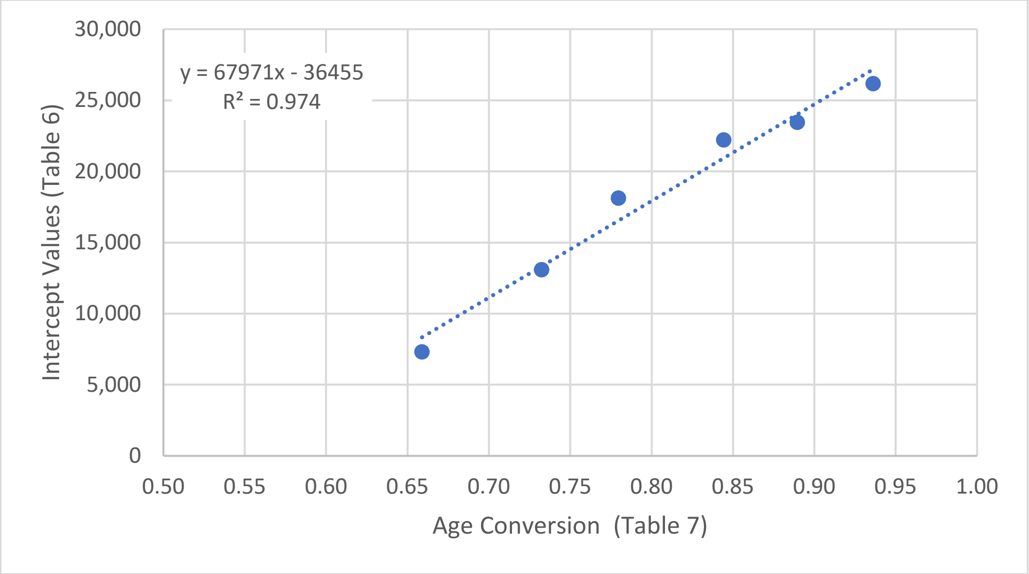


Figure 7—Age Conversion vs. Intercept

Figure 7 illustrates a good linear correlation ($R^2 = 0.974$) between the age conversion from Table 7 and intercept of the regression equation in Table 6. The slope values from Table 6 to the age conversion also produces a good correlation ($R^2 = 0.938$). These correlations indicate that Eqn. 12 is a good method to model age in days. The age in days is used to calculate the Age Factors (A_F) for the concrete mixtures used by Ore in Table 8.

The regression equation in Figure 7 can be used to estimate the age at which strength is equal to zero.
For $y = 0$, $X = (36455 \div 67971) = 0.53633$.
Transforming this value to age:
(Exp(exp(exp(0.53633))) ÷ 1000) = 0.2515 × 24 h = 6.04 hours.

For the Ore concrete mixtures, the calculated average strength for concrete with no air based on Eqn. 11 at various ages are shown in Table 8. The corresponding age factor (A_F) values from Table 7 are also shown. The ultimate strength of 8159 psi is a calculated value. Using an excel function “forecast” this ultimate strength is based on the values in column B and C. This the same as predicting the ultimate strength using a linear regression equation using X = values in column B and Y = values in column C. The ultimate predicted strength at 3814 days (10 years) is 8159 psi.

The average w/c ratio of the eight concrete mixtures for the Ore control concretes is 0.50. If a producer uses a set of control concrete mixtures with an average w/c of 0.50 for their calibration mixtures with portland cement only, ultimate strength value of 8159 psi can be used as a benchmark value to evaluate the effects of aggregate and cement combinations. A value exceeding this benchmark value indicates that a combination of materials will produce a potentially higher strength.

The value of 8159 psi will be referred to as the Strength Index. This can be used as a basis to compare performance, but not the cost of materials. If Producer A has an indicator of 8500 psi with a higher materials cost than Producer B with an indicator of 7500 psi; Producer B may be able to produce a more economical mixture (lower cost) than Producer A to produce concrete with an average strength of 5000 psi.

Table 8—Age Factor, A_F, for Concrete Strength Data from Ore

A Age, Days	B Age Conversion Table 7	C S_{NoAir} Eqn. 11	D S_{NoAir} ÷ Strength Index	E $A_F = (\text{Col D})^{1/3}$
1	0.659	1108	0.1358	0.5140
3	0.733	2150	0.2635	0.6411
7	0.780	3148	0.3859	0.7280
28	0.844	5083	0.6229	0.8541
90	0.890	6104	0.7481	0.9078
365	0.936	6576	0.8059	0.9306
3814	1.000	8159**	1.0000	1.0000

** Ultimate Strength Index – a calculated value

CONCRETE STRENGTH MODEL PREDICTION EQUATIONS

In this phase the cementitious gel portion of the cement paste that contributes to strength producing properties is quantified. It is assumed that calcium hydroxide is about 25% of the mass of hydrated cement with a specific gravity of 2.24. Powers[4] states that the cementitious gel has an average density of 2.65.

For 100 lb. of completely hydrated cement paste:
The volume of the cementitious gel = $[75 \div (2.65 \times 62.4)] = 0.454\ ft^3$
The volume of calcium hydroxide = $[25 \div (2.24 \times 62.4)] = 0.179\ ft^3$
The total volume is then $0.454 + 0.179 = 0.632\ ft^3$
The calcium hydroxide volume fraction is $(0.179 \div 0.632) = 0.28$
The volume fraction of cementitious gel = $(1 - 0.28) = 0.72$.

The numerator part of Eqn. 2 is ($2.06\ H_C\ C_V$). The volume of the cementitious gel is 0.72 times 2.06 = 1.477. Eqn. 13 determines the volume of hydrated cement that is the cementitious gel.

$$X_{Mix} = A_F\ H_U\ 1.477\ C_V \qquad \text{Eqn. 13}$$

Where:
A_F is the age factor
H_U is the ultimate hydration in Eqn. 7
C_V is the volume of cement in ft^3

To illustrate this: Assume water content = 300 lbs; cement content = 600 lbs; w/c = 0.50.
H_U based on Eqn.7 = $0.50 \div (0.50+0.17) = 0.746$.

Age Factor (A_F) for 28 days from Table 8 = 0.8541.
Volume of cement (C_V) = [600 ÷ (3.15 × 62.4) = 3.05 ft^3.
Using these values in Eqn. 13:

$$X_{Mix} = 0.8541 \times 0.746 \times 1.477 \times 3.05 = 2.87 \qquad \text{Eqn.14A}$$

An alternate calculation is equation No. 14B

$$X_{Mix} = 0.8541\times 0.746 \times 600 \times 1.243 \div 2.65 \div 62.4 = 2.87 \qquad \text{Eqn. 14B}$$

Eqn. 14B uses the cement content of 600 lbs and divides by the specific gravity of cementitious gel, 2.65. The factor 1.243 is (1 + the theoretical w/c to fully hydrate the cement, W_O. Eqn. 14A and 14B produce the same result using a value of 0.243 as the intrinsic amount of water that reacts with the cement, i.e., $W_O = 0.243$. For comparison this is the same amount of water in the calcium hydroxide, $Ca(OH)_2$. The molecular weight of $Ca(OH)_2$ is 74 and that of water is 18. The water is (18 ÷ 74) = 0.243 parts of the calcium hydroxide.

Eqn. 14B can be used to calculate the amount of original cement of 600 lbs that reacts at 28-days:
(0.8541 × 0.746 × 600 = 382.3 lbs).

The volume of hydrated cementitious gel that contributes to strength is
(382.3 × 1.243÷ 2.65 ÷ 62.4) = 2.87 ft^3

The equations used in this model to predict strength.

$$S_P = S_{NoAir}\, A_A \qquad \text{Eqn. 15}$$

Where:
S_P is the predicted strength
$A_A = (1 - A)^3$ Eqn. 16
A is the decimal percent air content in 1 cubic yard

$$X_{Mix} = [(A_F \times H_U \times C_W \times 1.243 \div 2.65 \div 62.4) \div (27\text{-}A)]^3 \qquad \text{Eqn. 17A}$$

Where:
A_F and H_U defined earlier
C_W is the weight of cement in lbs
A is the volume of air in ft^3 for a cubic yard

$$S_{NoAir} =[(\mathrm{Ln}(X_{Mix}) \times \mathrm{Slope}_{age}) + \mathrm{Intercept}_{age}] \qquad \text{Eqn. 18}$$

All the values used in Eqns. 15, 16, 17A, and 18 are mixture quantities based on yield determined from the unit weight; including gravimetric air content.

Table 9—Slopes and Intercepts for Concrete Strength Data from Ore with A_F from Table 8

Age, Days	Slope	Intercept	R^2	Prediction Error, psi (% of Avg)
1	1085	10546	0.9827	48 (5.1)
3	1918	17550	0.9890	69 (3.7)
7	2625	23233	0.9819	99 (3.6)
28	3007	24651	0.9866	120 (2.7)
90	3044	27383	0.9722	191 (3.6)
365	3446	30403	0.9539	273 (4.8)

The slopes are the same as in Table 6. The intercepts have changed with the inclusion of the Age Factor, A_F, from Table 8. The prediction error at 28-days of 120 psi is essentially the same as the error of 118.6 psi in Table 4. This is attributed to rounding off numbers. Eqns. 15 through 18 will be modified as needed as new materials are added. The primary difference will be changes of Eqn. 17A.

MODELING CONCRETE AGGREGATES

Tables 10 and 11 below summarize the aggregate constants calculated for the model. Three values for each set of aggregates: slope, intercept, and a strength index (S_{Index}).

Table 10—Intercepts for Aggregates

Report	w/c	S_{Index}	1-day	3-day	7-day	28-day	70-day	90-day	365-day
Region-3	0.382	8286	9548	17671	21526	21033		27766	
Region-2	0.568	7788	20589	24067	25536	28907		31714	
Region-4	0.571	7605	11788	19397	21836	25191		26540	
Region-1	0.622	7543	13175	16593	19084	24122		28620	
Region-5	0.661	6552	11059	13792	15378	19951		23167	
von Fay	0.620	7297			18377	22023		24586	24970
Ore	0.500	8159	10546	17555	23232	26650		27383	30403
NRMCA	0.507	9013			16295	15784	17443		

Table 11—Slopes for Aggregates

Report	w/c	S_{Index}	1-day	3-day	7-day	28-day	70-day	90-day	365-day
Region-3	0.382	8286	920	1872	2314	2181		3061	
Region-2	0.568	7788	2387	2841	3019	3452		3834	
Region-4	0.571	7605	1255	2191	2487	2904		3046	
Region-1	0.622	7543	1446	1845	2149	2788		3429	
Region-5	0.661	6552	1190	1515	1692	2283		2650	
von Fay	0.620	7297			2266	2502		2803	2835
Ore	0.500	8159	1085	1917	2625	3007		3044	3445
NRMCA	0.507	9013			1773	1539	1746		

The data by Ore[10] has been used extensively in this report. These data include concrete mixtures with and without water reducing admixture (WRA). These data are used to discuss the effect of water-reducing admixture (WRA) in the next section.

The data from von Fay[7] is from the USBR in the 1980's. These data include concrete mixtures with portland cement at several w/c ratios; and with fly ash at five percentages at two different total cementitious contents. These data are used to evaluate the effect of fly ash in a later section.

The data named by Region is from Dunstan[6] from work funded by EPRI. These represents mixtures prepared with materials in 5 regions of the US. The data are for concretes with and without air entrainment and with and without WRA. These mixtures contain 17 fly ash sources available in those regions. These data were used to validate the overall model in the section on fly ash in a later section.

It is recognized in this model that the cement reaction establishes a basis for the strength model. Control concrete mixtures to establish the model parameters must include strength data for mixtures at several w/c ratios.

The NRMCA data was developed specifically for this project. These mixtures include portland cement, with no WRA and no fly ash as the base mixtures to calibrate the model. The mix designs and strength results are in Appendix 2. The NRMCA data is an important element in developing the model as shown in Tables 10-11. Because the impact of aggregates will vary, the model must establish constants for the aggregates. It is observed that the aggregate used in the NRMCA study has much different properties than that in the other sets of data.

To evaluate the effect of aggregates, the average w/c of the concrete mixtures used for calibrating the model are compared to the calculated Strength Index for each aggregate. This trend is shown in Figure 8. The general trend is the Strength Index increases as the average w/c ratio decreases.

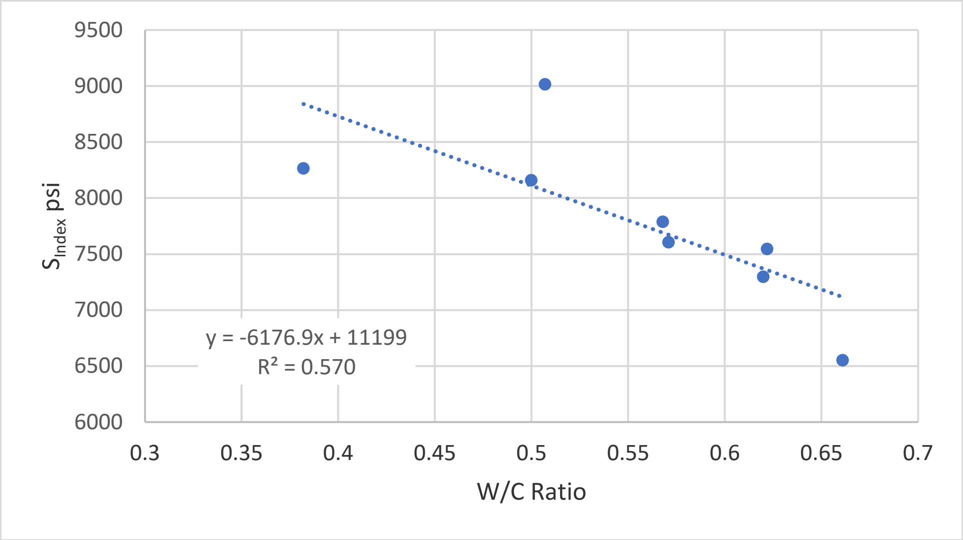


Figure 8—w/c ratio vs. Strength Index, S_{Index}

To normalize the values in Tables 10 and 11, it is suggested that the average w/cm of calibration mixtures with portland cement should be 0.50. This will permit the use of the strength index to compare the effects of aggregates. Consider, the regression constants for NRMCA and Ore in Tables 10 and 11. These two sets of data have an average w/c of 0.50. The aggregates used by NRMCA produces higher strength index - 9013 psi versus 8159 psi for Ore. Notice that the slopes and intercepts for the NRMCA aggregate are smaller than the slopes and intercepts values for the Ore concretes. It was observed that the aggregates used in the NRMCA study had significantly different characteristics. The slope variable for the NRMCA aggregate are almost constant with age, whereas for the other data sets, the slope variables increase with age. Could this be related to the bond of cement paste with the aggregate?

It is also suggested in future work several aggregates should be used in the calibration mixtures at an average w/c of 0.50. The mixtures should use the same cement, no WRA and should be non air-entrained. This may suggest something about the effect of aggregate bond and aggregate strength when observing trends of slope with age, intercept with age, and Strength Index with the same cement.

Another interesting comparison is observed when comparing the data of von Fay and Ore. These concrete mixtures contain the same aggregates and at the same grading. The difference is the cement used. Can the model also separate out the effect of cement? In future aggregates work, the same cement can be used to describe aggregates and a change in cement with the same aggregate can model the effect of cement.

The Strength Index will be shown to be a significant number in the next section which discusses the use of WRA and changes in WRA dosage. Strength Index also changes as the mixing temperature is changed from 50° to 73° to 90°F.

CONCRETES CONTAINING CHEMICAL ADMIXTURES

Consider Eqn. 7 discussed earlier in this paper.

$H_U = (w/c) \div [(w/c) + 0.17]$ Eqn. 7

Where 0.17 is the water in the gel pores.

The following is a modification of Eqn. 7.

$H_C = (w/c) \div [(w/c) + H_{Index}]$ Eqn. 7A

Where:
H_C Is a Hydration Coefficient
H_{Index} is an all-encompassing Hydration Index

When $H_{Index} = 0.17$, hydration is as expected and predicted by using bound water, in accordance with the procedures of Mills[14] and Powers[4]. It is demonstrated H_{Index} is a lower value in mixtures that contain water reducing admixtures (WRA) for strengths at all ages. Assuming that the WRA disperses cement particles and the gel water content is reduced, the value of H_{Index} will be less than 0.17. For mixtures containing only portland cement with no chemical admixture, with a w/c of 0.50 the ultimate cement hydration is $0.50 \div (0.50 +0.17) = 0.746$. If chemical admixture disperses the cement and the gel water is lowered to 0.15 the ultimate hydration is increased $0.50 \div (0.50 +0.15) = 0.769$, thereby increasing the degree of hydration at all ages. The amount of water in gel pores is an indicator of the amount of cement that hydrates. A lower amount of gel water indicates that there is less cement that is entrapped and will not hydrate. Thus the degree of hydration increases when the gel water indicator is reduced. Concrete mixtures containing chemical admixtures will normally have an H_{Index} lower than 0.17 and decreases as the dosage of chemical admixture increases.

Concrete Mixtures with water reducing admixture (WRA) from Ore[10]

For the mixtures made by Ore, the H_{Index} value of 0.17 was used to develop the slopes and intercepts in Table 9. A lignosulfonate-based water reducing admixture was used. The dosage rates used at four different levels were 3.2, 6.3, 9.5 and 12.7 oz/cwt. The average water content for the mixtures without WRA was 244.5 lb/yd^3. The average water content for the mixtures with WRA 243.5, 239.6, 234.5, and 231.4 lb./yd^3, respectively. $H_{Index} = 0.17$ was initially assumed for the mixtures with WRA. Based on this assumption, using the slope and intercepts of Table 9, the predicted strength of the mixtures with WRA are lower than the measured strength. This indicates that the resulting water reduction does not fully account for the strength of mixtures with WRA.

In Table 12, the calculated H_{Index} values are indicated for the Ore concrete mixtures containing WRA. The values were back calculated from the measured strengths using the Eqn. 15 through 18 with Eqn.17A modified based on Eqn. 7A to Eqn. 17B:

$X_{Mix} = [(A_F \times H_C \times C_W \times 1.243 \div 2.65 \div 62.4) \div (27-A)]^3$ Eqn. 17B

Where H_U from 17A is replaced with H_C from Eqn. 7A:

The $H_{Index} = 0.17$ for mixtures without WRA and less than 0.17 for mixtures with WRA.

The slope and intercept used are those for the control concrete mixtures with no WRA in Table 9. A_F is based on the average strengths and strength index = 8159 psi for mixtures with no WRA at each age and calculated using values in columns C, D, and E in Table 8. Using the measured strength of the mixtures with each dosage of WRA the Strength Index is calculated and reported in Table 12. The measured strength was adjusted to the strength with no air based on Eqn. 11. X_{Mix} is calculated using Eqn. 18. This is followed by calculating H_C using Eqn. 17B. Using this value of H_C, H_{Index} is calculated using Eqn. 7A.

Table 12—H_{Index} and Strength Index for Ore[10] Concrete Mixtures with WRA

	WRA Dosage, oz/cwt				
	0	**3.2**	**6.3**	**9.5**	**12.7**
H_{Index}	0.1700	0.1588	0.1400	0.1178	0.1093
Strength Index	8159	8594	8743	9068	9098

The values for H_{Index} in Table 12 are constant for all ages for each dosage level of WRA. H_{Index} decreases as the dosage of WRA increases further illustrated in Figure 9. The calculated Strength Index increases as the dosage of WRA increases. This indicates that WRA causes an increase in strength more so than that resulting from a reduction in water content.

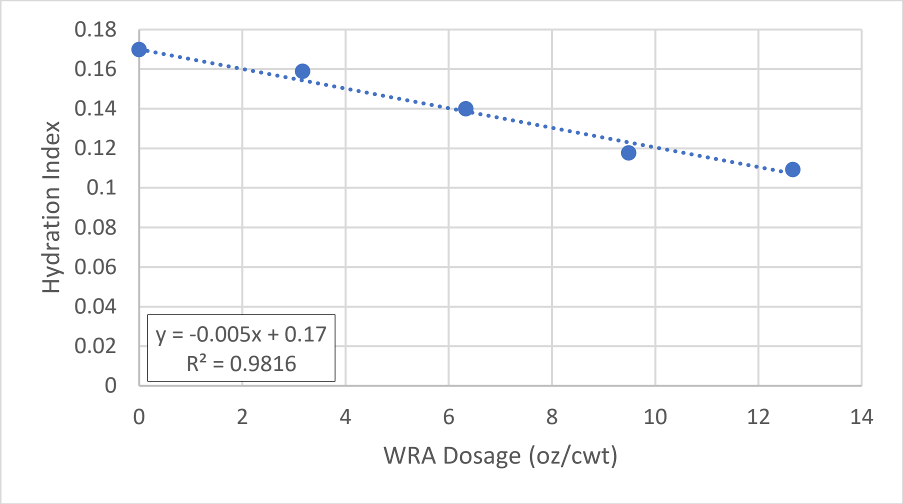


Figure 9—Hydration Index (H_{Index}) Versus WRA Dosage (oz/cwt)

EFFECT OF CONCRETE TEMPERATURE

Ore[10] also cast concrete mixtures with w/cm of 0.50 at an initial temperature of 90°F and 50°F. The values for H_{Index} and Strength Index are shown in Table 13 for mixtures cast at these temperatures and compared to the values for mixtures cast at 73°F from Table 12.

Table 12—H_{Index} and Strength Index for Ore[10] Concrete Mixtures with WRA at different mixing temperatures

		WRA Dosage, oz/cwt				
		0	**3.2**	**6.3**	**9.5**	**12.7**
H_{Index}	90°F	0.2043	0.1971	0.1836	0.1366	0.1295
	73°F	0.1700	0.1588	0.1400	0.1300	0.1093
	50°F	0.1696	0.1374	0.1169	0.1181	0.1068
Strength Index	90°F	8266	8253	8503	8778	8678
	73°F	8159	8593	8744	9067	9097
	50°F	8782	9450	9362	9076	9213

For concrete mixtures with no WRA, the H_{Index} is greater than 0.17 at 90°F and less than 0.17 at 50°F. For mixtures with WRA, the H_{Index} is greater at higher temperature and lower at the lower casting temperature.

It is generally recognized that concrete produced at higher temperatures will have lower ultimate strengths and those at lower temperatures will have higher ultimate strengths. In most cases, the Strength Index values for the concrete mixtures cast at 90°F have lower values to those cast at lab temperature and the value is greater for the mixtures cast at 50°F. In summary, the addition of WRA reduces the H_{Index} and increases the Strength Index in a similar effect to temperature.

At the highest dosage of WRA (12.7 oz/cwt) the H_{Index} is approximately 64% of that of the mixture without WRA at all temperatures. For all ages the strength index increases as the temperature of mixing decreases. Mixtures at varying temperatures were only evaluated with a w/c = 0.50. For the control mixtures at w/c of 0.50, the average water content was 234 lbs/yd^3. For this mixture at 90°F the water content was 256 lbs/yd^3 and it was 235 lbs/yd^3 at 50°F. At the maximum WRA dosage the water demand to 231 lbs/yd^3 at 90°F and 219 lbs/yd^3 at 50°F.

Earlier it was suggested that the amount of entrapped cement that does not react is directly related to the amount of gel water. Does concrete mixed at elevated temperatures have a higher H_{Index} value indicating more entrapped gel water and thus more entrapped cement? Does the higher temperature speed up the setting and seal off more cement so that it does not hydrate whereas lower temperature concretes take longer to set and allows more time for the water to reach and hydrate more of the cement?

The Strength Index captures the effect of WRA dosage and temperature at mixing. The Strength Index for 73°F increases as the WRA dosage increases and the same trend is seen for concrete mixed at 90°F and 50°F. The Strength Index also increases as the batching temperature is changed from 90°F to 50°F. In summary, lower temperature at batching with a higher WRA dosage gives the highest strengths.

The H_{Index} decreases as the WRA dosage increases. For mixtures with no WRA, H_{Index} decreases as batching temperature decreases. The H_{Index} for each WRA dosage at 73°F from an average for eight concrete mixtures. For concrete batched at 90°F and 50°F, H_{Index} is based on single concrete mixture. So, there is some uncertainty associated with this parameter.

Figure 11 is a plot predicted vs. measured strength of all the mixtures with and without WRA and includes 240 data points. It is suggested that prediction errors are associated with batching, mixing, casting cylinders, and strength testing. Prediction errors increase at later ages, for strength exceeding 7000 psi. This suggests that the predicted strength gain, estimated from bound water hydration, is slightly greater than that of the measured strengths. It was noted earlier that a model based on hydration (bound water) will have the largest errors for ages greater 56 days (higher strengths). The overall average measured strength of at all ages is 3700 psi and the average of the predicted strengths was 3794 psi.

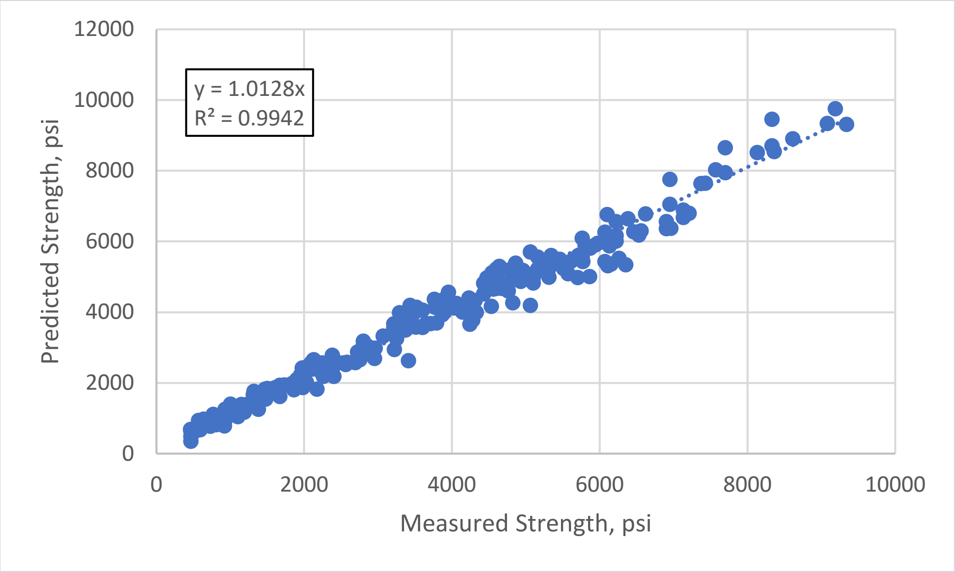


Figure 11—Measured Versus Predicted Strength (Concrete at 73°F)

Table 14 below shows calculated values for H_{Index} for various WRA dosage for the sets of concrete mixtures included in this report.

Table 14—H_{Index} for 7 sets of Concrete Mixtures

Concrete Data Set	Number of Mixtures	WRA Dosage Oz/cwt	H_{Index}
Ore	8	3.17	0.1588
Region 1	4	3.60	0.1177
Region 2	4	3.54	0.0878
Region 3	4	3.52	0.1422
Region 4	4	4.40	0.1252
Region 5	4	3.28	0.0945
NRMCA	2	3.00	0.0803

For all concrete mixtures containing a WRA the value of H_{Index} is less than 0.17. It was shown earlier that H_{Index} decreases as the dosage of WRA increases (Figure 10). The H_{Index} can be predicted as WRA dosages vary from those in Table 14. For example, one concrete mixture with a WRA dosage of 6 oz/cwt in the NRMCA series had a H_{Index} of 0.0335. Values for H_{Index} for the NRMCA mixtures are plotted in Figure 12.

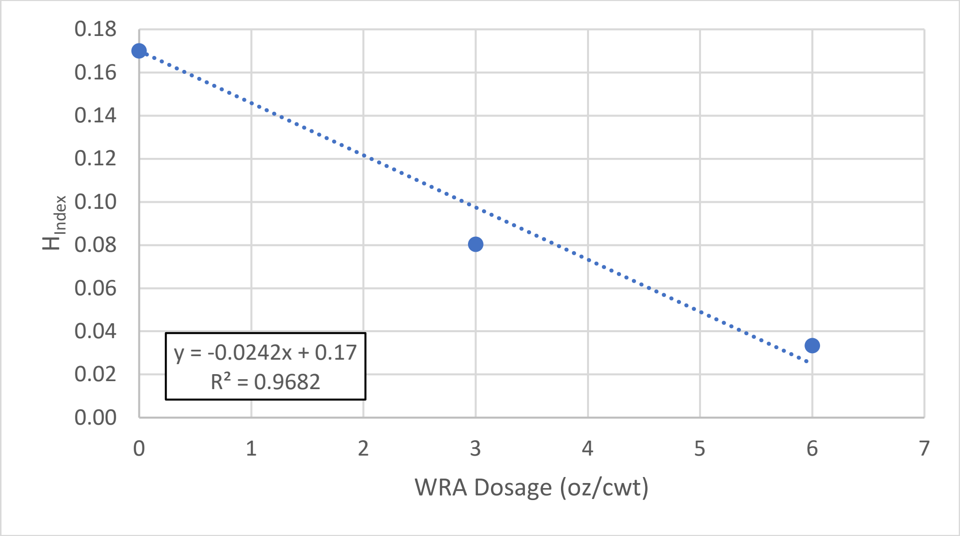


Figure 12—H_{Index} Versus WRA Dosage for the NRMCA Concrete Mixtures

The NRMCA data confirms that as the WRA dosage increases there is a linear decrease in the value for H_{Index}.

STRENGTH MODELLING OF CONCRETES WITH POZZOLANS (FLY ASH)

The following is a quote stated earlier from Baker/TSA[5] is repeated:

> *Based on previous research, Dunstan developed relationships for estimating the compressive strength of cured concrete from a fly ash "lime affinity" factor and "equivalent cement" parameters. The resulting predictive equations are extensive modification of Feret's equation for concrete strength and include considerations of fly ash content, the available lime released by cements, maturity of the lime-fly ash reactions and the cementitious characteristics of fly ashes.*

The two concepts outlined in the above quote are (1) *lime affinity* and (2) *equivalent cement*. The broader term *equivalent cement* includes the pozzolanic reaction (lime affinity) and self-cementing reactions. Self-cementing reactions are those in which the CaO content of the fly ash hydrates to produce strength. Later, fly ash reactions will be separated into (1) pozzolanic and (2) self-cementing reactions. However, the historical cement equivalent also includes (3) strength due to water reduction and (4) strength due to filler effect.

Previously, contribution of fly ash has been modeled using a fly ash index[18] with a value between 0 and 1. The value 0 is for no hydration and 1 is when 100% of the fly ash has reacted. This is similar to a cement equivalent.

What is *cement equivalent*? Smith[22] developed a "K" value for cement equivalent (C_{EQ}) in 1967 and this author has previously described this value as fly ash efficiency[12].

Consider the following equations which are modified to include the term C_{EV} which is a fly ash value--cement equivalent volume. The volume of fly ash that reacts forms hydrate products similar to cement. This calculated volume is considered to be equivalent to a volume of cement that would hydrate to produce that volume – an equivalent cement volume, C_{EV}.

$S_P = S_{NoAir} A_A$ Eqn. 15

Where:
S_P is the predicted strength
$A_A = (1 - A)^3$ Eqn. 16
A is the decimal percent air content in 1 cubic yard

$X_{Mix} = [\{(A_F \times H_C \times C_W \times 1.243 \div 2.65 \div 62.4) + C_{EV}\} \div (27\text{-}A)]^3$ Eqn. 17B

Where:
A_F is the age factor
H_C is a hydration coefficient

$H_C = (w/c) \div [(w/c) + H_{Index}]$ Eqn. 7

C_W is the weight of cement in lbs/yd^3
A is the volume of air in ft^3 for a cubic yard
C_{EV} is cement equivalent volume

$C_{EV} = C_{EQ}\ P_W \div 2.65 \div 62.4$ Eqn. 20A

C_{EQ} is the cement equivalent

$C_{EQ} = C_{EV} \times 2.65 \times 62.4 \div P_W$ Eqn. 20B

$S_{NoAir} = [(\mathrm{Ln}(X_{Mix}) \times \mathrm{Slope}_{age}) + \mathrm{Intercept}_{age}]$ Eqn. 18

Fly Ash and Hydration Index

Consider the following equation for H_{Index} which varies relative to filler effect:

$H_{Index} = [(1 - (F_X \times P\% \times (w/(c+p))] \times 0.17$ Eqn. 19

0.17 is the H_{Index} with no WRA
F_X is a decimal percent filler constant; assume $F_X = 1.0$
P% is the decimal percent of fly ash
w is the weight of water lbs/yd^3
c is the weight of cement lbs/yd^3
p is the weight of fly ash lbs/yd^3
w/(c+p) is the water to cement+pozzolan ratio

For mixtures with no fly ash or WRA, H_{Index} is 0.17 as in Eqn. 7. Water reducing admixtures disperse cement particles and reduce the amount of cement that is sealed off from potentially hydrating and reduces the value to less than 0.17. If fly ash added, these particles change the internal structure creating pathways for water to hydrate more cement. As fly ash increases it increases the amount of cement that can hydrate and reduces the amount of cement trapped and sealed off in the gel. Liu et.al.[23] indicate an increase in cement hydration due to fly ash (referred here as the filler effect). The filler effect is directly related to the volume of fly ash. As the percent of fly ash increases the hydration of cement is increased. The filler effect is related to the w/(c+p) ratio as shown in Eqn. 19. As the w/(c+p) ratio increases the filler effect increases.

Massazza[24] provides several references to research that states that cement hydration (C_3S) increases in mixtures containing fly ashes. He references research with 25% fly ash content in which the cement hydration at 28-day for four different cement increased by 3 to 9 percent. He also references studies showing that accelerating effect increases with an increased amount of fly ash and this effect varies depending on the type of fly ash. In this model, a single value for H_{Index} for all fly ashes from Eqn. 19. If P% = 0.25 and the w/(c+p) = 0.50, H_{Index} from Eqn. 19 = 0.1488.

Without fly ash, Eqn. 7 determines the ultimate hydration = 0.50 ÷ (0.50 + 0.17) = 0.746. With H_{Index} = 0.1488 ultimate hydration = 0.50 ÷ (0.50+0.1488) = 0.771. This suggests an increase in cement hydration by 3.35% (0.771÷0.746). Liu et.al.[23] used a hydration value for cement of 0.23 versus 0.243 used here. They also used a hydration value for the fly ash of 0.168, while a value of 0.157 is assumed here. How would these numbers change the values of Liu? The filler effect by Liu (50% fly ash and w/(c+p) = 0.50) was an increase of cement hydration of approximately 3.75% whereas Eqn. 19 suggests 3.35%. These estimates, 3.35% and 3.75%, are at the low end of the range suggested by Massazza[24] of 3 to 9 percent. Filler effect is physical and will vary based on the synergy of the particle size distribution of the fly ash and that of the cement. In this model, the filler constant, F_X in Eqn. 19 is assumed as 1.0. Is there a method to calculate F_X?

Using filler effect values in Eqn. 19, indicates that C_{EQ} values for fly ashes are basically the same for concrete mixtures containing fly ash with varying w/(c+p). If the filler effect is ignored and setting $H_{Index} = 0.17$, C_{EQ} values varied significantly with w/(c+p). The C_{EQ} values for fly ash shown later in this report are assumed to be the same at all levels of w/(c+p). As the materials used in concrete mixtures increases, such as WRA, and then fly ash, the prediction error increases. To reduce this error, the number of concrete mixtures used for calibration must be increased to obtain a representative average.

There is an additive effect of using WRA and fly ash. In Eqn. 19, if the concrete contains a WRA H_{Index} varies based on WRA dosage as in Table 14. H_{Index} decreases with the use of WRA and further decreases by the addition of fly ash. The assumption here is that fly ash and WRA cause dispersion of cement particles and increase the degree of hydration.

The factor F_X in Eqn. 19 is used for the filler effect which was derived to produce a fly ash C_{EQ} that has the least variation with changes in w/(c+p). It is assumed that for a specific fly ash, C_{EQ} is a constant and it is the same at all w/(c+p).

There is current research on use of nanoparticles that increase the hydration of cement and increase in strength. Strength increases are observed with injection of carbon dioxide into concrete – that results in the precipitation of fine calcium carbonate that changes the internal structure. Inter-grinding of limestone with cement clinker will have a filler effect. Does the value of H_{Index} decrease from 0.17 for cement with inter-ground limestone? In theory, this internal physical addition disperses cement particles, opens up the physical structure of hydrating paste and exposes more cement to hydration. Strength is a third power function. So if strength is increased by 10% that is $1.10^{(1/3)} = 1.032$ suggests that the H_{Index} has been reduced to produce 3.2% increased hydration.

Fly Ash - Cement Equivalent

C_{EV} can be calculated using the above equations. The strength of concrete containing a fly ash will be higher than that predicted based on the quantity of water and cement in the mixture.

For example, considering the volume of cement only in Eqn. 17B, the volume of hydrated cement would be $(1.243 \times A_F \times H_C \times C_W \div 2.65 \div 62.4)$.
If the volume of cement in a concrete mixture = 1.62 ft^3 and the total volume of hydrated product is 1.80 ft^3, then $C_{EV} = (1.80 - 1.62) = 0.18$ ft^3.
Assume the weight of fly ash = 85 lbs/yd^3.
The equivalent cement weight (C_{EQ}) = $0.18 \times 2.65 \times 62.4 \div 85 = 0.350$ (from Eqn. 20B).

The volume of hydrated product of 1.80 ft^3 is from back calculation.
Using the measured strength of the concrete mixture, calculate the strength with no air (S_{NoAir}) using Eqn. 11.
Calculate $Ln(X_{Mix})$ using Eqn. 13 from which the total volume X_{Mix} can be calculated:
$X_{Mix} = [\{Exp(Ln(X_{Mix})]^{(1/3)}\} \times (27\text{-}A)$.

This is based on a simple concept. It was first introduced by Smith[18]. This concept of cement equivalent was used in in two recent publications[12, 25]. In one, the cement equivalent was called fly ash efficiency[25] and in the more recent reference[12] it is referred to as strength efficiency. These references did not consider the effect of increased cement hydration due to a fly ash or pozzolan (filler effect). References that state a K-value are likely greater than the cement equivalent values in this model, because K values in the references include the increase in cement hydration (filler effect) as part of fly ash reaction.

Table 15 includes calculated values for C_{EQ} for all of the concretes containing fly ash evaluated by the model equations discussed above. The source of the fly ashes are identified in Appendix 3.

Table 15—Calculated Values for C_{EQ} for the Concretes Data Sets for This Model

Data Set (# Mixes)	Ash # – CaO%	% Ash	Calculated Values for C_{EQ}						
			1-Day	3-Day	7-Day	28-Day	70-Day	90-Day	1-Year
von Fay (2)	#1-10.9	10			0.3722	0.4010		0.4669	0.8516
von Fay (2)	#1-10.9	30			0.5055	0.5840		0.7176	0.7616
von Fay (2)	#1-10.9	50			0.5099	0.5449		0.6789	0.7450
von Fay(2)	#1-10.9	75			0.4844	0.5014		0.5720	0.6350
von Fay (2)	#2-21.1	10			0.7333	1.0211		0.8714	1.0485
von Fay (2)	#2-21.1	30			0.5609	0.6773		0.7646	0.8885
von Fay (2)	#2-21.1	50			0.5834	0.6553		0.8139	0.9634
von Fay (2)	#2-21.1	75			0.4679	0.5586		0.6541	0.8140
von Fay (2)	#3-28.6	10			0.9210	1.3061		1.1848	0.9542
von Fay (2)	#3-28.6	30			0.6986	0.8161		0.7851	0.9365
von Fay (2)	#3-28.6	50			0.6108	0.7287		0.7344	0.8446
von Fay (2)	#3-28.6	75			0.4474	0.5990		0.7000	0.7878
Region-1 (3)	#4-2.64	15	0.2620	0.3494	0.3347	0.3794		0.4482	
Region-1 (5)	#4-2.64	30	0.3647	0.4133	0.4274	0.5150		0.6874	
Region-1 (4)	#5-1.76	15	0.2460	0.2916	0.3713	0.2447		0.2952	
Region-1 (7)	#5-1.76	30	0.3664	0.3872	0.4234	0.4370		0.5323	
Region-1 (2)	#6-2.18	15	0.2239	0.2696	0.3000	0.1962		0.3541	
Region-1 (3)	#6-2.18	30	0.3551	0.4082	0.4350	0.4635		0.5875	
Region-2 (5)	#7-1.42	15	0.2835	0.3560	0.4768	0.6391		0.7170	
Region-2 (8)	#7-1.42	30	0.3650	0.4141	0.4656	0.6326		0.7458	
Region-2 (4)	#8-3.01	15	0.2093	0.2475	0.3522	0.3613		0.4250	
Region-2 (7)	#8-3.01	30	0.3768	0.4200	0.4393	0.4812		0.5720	
Region-2 (1)	#8-3.01	60	0.5262	0.5032	0.5215	0.5826		0.7894	
Region-2 (1)	#9-1.09	15	0.3778	0.4653	0.5179	0.5433		0.6020	
Region-2 (3)	#9-1.09	30	0.4382	0.4491	0.4595	0.5104		0.5981	
Region-3 (4)	#10-25.3	15	0.6025	0.3154	0.2789	0.7184		0.4602	
Region-3(9)	#10-25.3	30	0.3486	0.4451	0.4751	0.7364		0.8131	
Region-3 (2)	#11-15.0	15	0.3586	0.2691	0.2377	0.8095		0.3572	
Region-3 (3)	#11-15.0	30	0.2642	0.4072	0.4772	0.7769		0.7488	
Region-3 (1)	#11-15.0	60	0.2373	0.3691	0.4336	0.5950		0.6791	
Region-3 (4)	#12-4.9	15	0.2605	0.2246	0.1724	0.3731		0.4282	
Region-2 (4)	#12-4.9	30	0.2531	0.3687	0.4180	0.6283		0.6880	
Region-3 (1)	#13-27.6	15	0.2077	0.5141	0.5767	1.0067		0.6969	
Region-3 (3)	#13-27.6	30	0.1039	0.4912	0.5411	0.9548		0.7149	
Region-4 (2)	#14-5.4	15	0.1330	0.1559	0.1278	0.1384		0.2608	
Region-4 (4)	#14-5.4	30	0.3217	0.3800	0.3800	0.3963		0.4988	
Region-4 (1)	#14-5.4	60	0.4304	0.4845	0.4709	0.4808		0.4902	
Region-4 (4)	#15-26.0	15	0.2928	0.2370	0.2923	0.4025		0.5613	
Region-4 (6)	#15-26.0	30	0.3253	0.4341	0.4502	0.5435		0.6272	
Region-4 (1)	#15-26.0	50	0.4170	0.4592	0.4910	0.5737		0.8677	
Region-4 (3)	#3-29.5	15	0.2558	0.2432	0.2634	0.3478		0.3552	
Region-4 (3)	#3-29.5	30	0.4155	0.4464	0.4934	0.5754		0.6431	
Region-4 (1)	#3-29.5	50	0.3767	0.4918	0.5550	0.6498		0.7491	
Region-5 (6)	#1-10.6	15	0.1730	0.3002	0.2370	0.3041		0.2983	

Region-5 (4)	#1-10.6	30	0.3714	0.4753	0.5066	0.6046		0.7424	
Region-5 (2)	#2-22.3	15	0.3195	0.5510	0.5301	0.6419		0.6188	
Region-5 (5)	#2-22.3	30	0.3620	0.4536	0.5343	0.6807		0.7520	
Region-5 (3)	#16-10.9	15	0.1581	0.3034	0.1788	0.3178		0.2391	
Region-5 (7)	#16-10.9	30	0.3447	0.4712	0.4939	0.5692		0.6866	
NRMCA (4)	#17-???	20			0.0146	0.0592	0.5680		
NRMCA (1)	#17-???	40			0.3260	0.2372	0.5203		
NRMCA (1)	#17-???	70			0.3935	0.2343	0.2913		

An observed and expected trend in Table 15 is an increase in C_{EQ} results with age for all fly ash percentages. There are exceptions with 15% fly ash. There appears to be more variability in mixtures with 15% fly ash content compared to the 30% fly ash content. This is true for all levels of CaO. This variability may obscure the results. This translates to predicting strength for the 15% fly ash content will have larger prediction errors than at higher content.

When the primary fly ash reaction is pozzolanic (CaO at 5.4% and lower), C_{EQ} increases as fly ash content increases. This is relevant for fly ash in Regions 1 and 2 as well as for the low CaO fly ash, such as #12 in Region 3 and #14 in Region 4. This trend is the same as values calculated by Liu et.al.[23] for a low CaO fly ash when used at contents of 10% to 50%.

The results are mixed for fly ashes with higher CaO contents; in some cases C_{EQ} increases with fly ash content and in other cases it decreases as the fly ash content increases – in #11, #13, and in some cases the reduction shows up at fly ash percentages in excess of 30% such as ash #1 in the von Fay data. Is this trend an indicator of the level of pozzolanic reaction? If the pozzolanic reaction is minimal, is a reduction in C_{EQ} as the fly ash content increases an indicator of lower pozzolanic reaction? Fly ash with low pozzolanic reaction will have reduced benefits for durability, such as ASR or sulfate resistance.

The C_{EQ} values in Table 15 demonstrate that compressive strength is related to CaO content. This is illustrated in Figure 13.

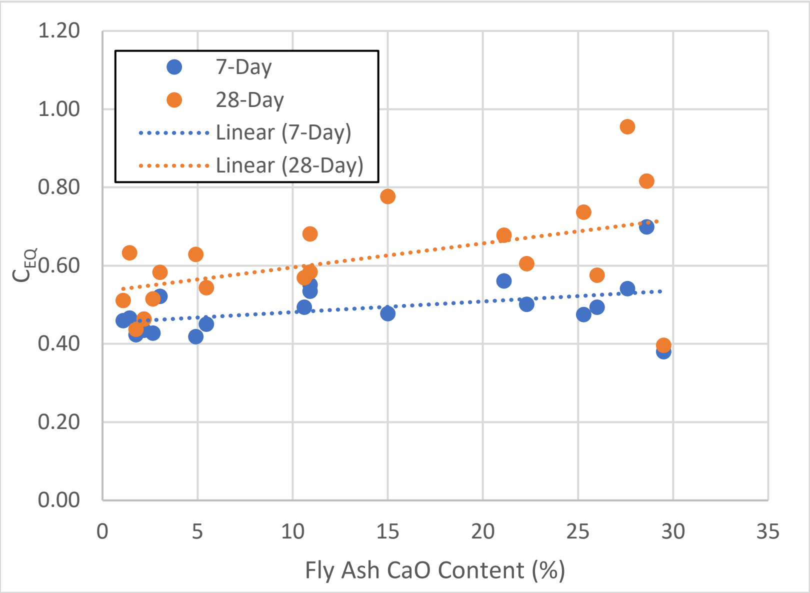


Figure 13—Fly Ash CaO Content Versus CEQ 7-Days and 28-Days' Age

The strength trend is more obvious by looking at each set of concrete mixes as shown in Figure 14.

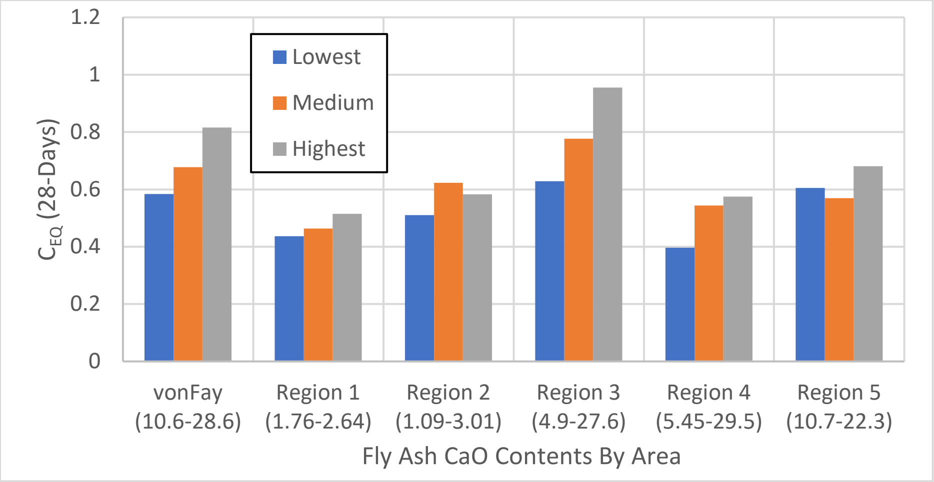


Figure 14—CEQ with CaO for 30% Fly Ash Content

In Figure 14, the C_{EQ} increases as the CaO content in fly ash increases. This figure also suggests that cements do not have the same magnitude of reaction with fly ash. All the fly ashes in Region 1 and 2 have a low CaO content, however the magnitude of C_{EQ} is greater for Region 2. This can indicate that this cement worked better with the fly ash. Similar differences can be observed comparing Region 4 and Region 5.

Cement chemistry does not necessarily show causes for differences in how it works with fly ash. Reasons could be related to filler effect or an alternative physical effect. It could be a synergy between the particle size distribution of the fly ash and cement or lack thereof. A potential future development of this model could improve the filler effect contributed by fly ash. This could address the behavior of fly ash with different cements.

Cements can be similar. Table 16 compares the 30% fly ash content with fly ash #1 and #2 in the von Fay data to that from Region 5.

Table 16—Comparing Fly Ash #1 and #2

Data Set	% Ash	C_{EQ}-7 Days	C_{EQ}-28 Days	C_{EQ}-90 Days
von Fay #1	30%	0.5055	0.5810	0.7176
Region-5 #1	30%	0.5066	0.6046	0.7424
von Fay #2	30%	0.5609	0.6773	0.7646
Region-5 #2	30%	0.5343	0.6807	0.7520

The cement used for the von Fay data is likely much different than the cement used in Region 4 data. There are significant differences when comparing fly ash #3 in the von Fay data to Region 4 data. The same fly ashes were used in these two studies, however, the C_{EQ} values are significantly different, possibly due to a change in the filler effect with the different cements.

The last set of C_{EQ} values in Table 15 are for the NRMCA data. These values are significantly different than all the other values. In the aggregates section of this report the slope and intercept values were much different for the NRMCA data compared to that for the other sets of data using various different aggregates. The aggregate used by NRMCA is hard and dense. Does this impact the paste bond with this aggregate and does this impact the values for the NRMCA data in Table 15? Additional research is needed to evaluate the use of fly ash with this aggregate.

Prediction Error for Fly Ash Mixtures

The prediction error for the model has not been determined for all the data sets with fly ash in Table 15. Figure 15 shows the prediction error for one set of concrete mixtures for fly ash #1, Region 5. The data points in Figure 15 are for strengths at 1, 3, 7, 28 and 90-days and include the control concrete mixtures with no

WRA and fly ash; the mixtures with WRA; and the mixtures with fly ash at 15 and 30% content from Table 15.

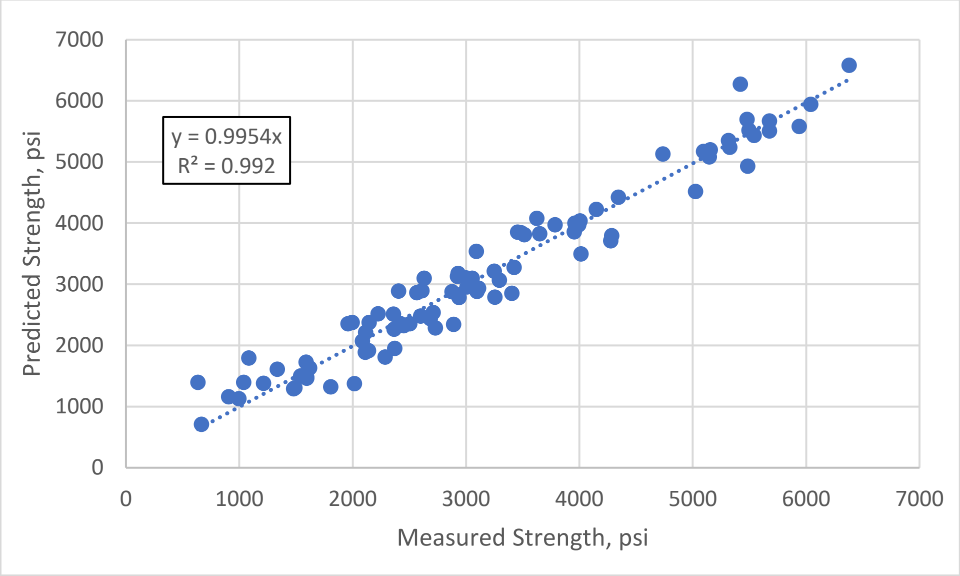


Figure 15—Prediction Error – Mixtures with Region 5-Fly Ash #1

The average measured strength of all mixtures = 3160 psi and the average of predicted strengths is 3163 psi. The average prediction error is 242 psi. This is considered a good prediction.

Fly Ash – Separating Self-Cementing and Pozzolanic Reaction

The von Fay data includes three fly ashes at different CaO contents of 10.9%, 21.1% and 28.6%. Each fly ash was used in 10 concrete mixtures with fly ash contents of 10%, 30%, 50%, 75% and 100%. Each fly ash was used at two different total cementitious contents of 424 lb/yd^3 and 645 lb/yd^3. The concrete strengths were measured at 7, 28, 90, and 365-days.

For many mixtures, the strength was minimal at 100% fly ash content and could not be tested. Concrete mixtures with the 28.6% CaO fly ash produced measurable strengths at an age of 365 days: 1805 psi in mixtures with 427 lb/yd^3; and 4665 psi with 652 lb/yd^3. Considering the fly ash as cement in this model and comparing with control concrete mixtures, this fly ash produced about 70% of the strength as a mixture with portland cement only.

The author has compared the chemistry of fly ash to slag in an earlier publication[11]. Figure 16 is from that reference.

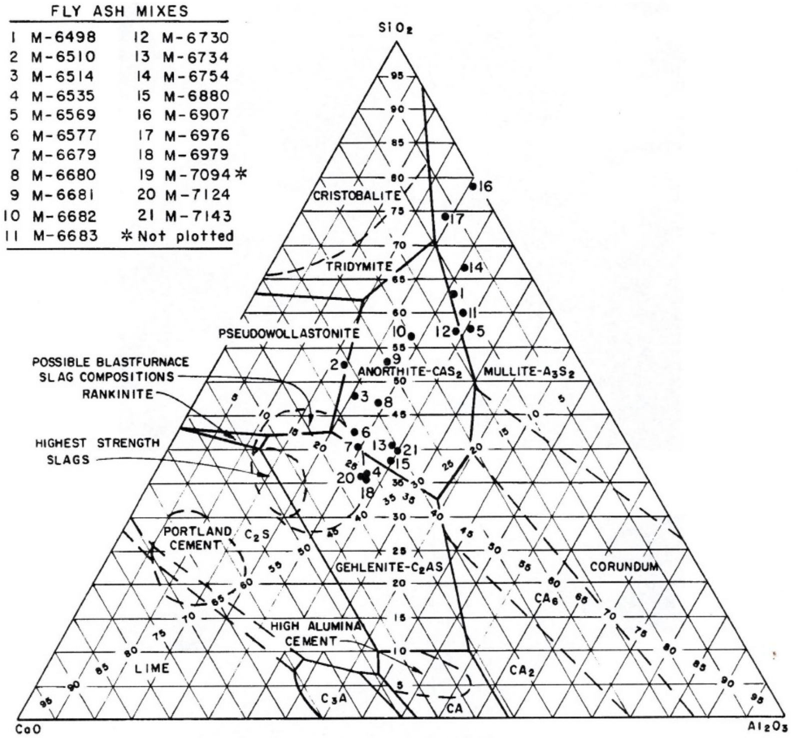


Figure 2. — Relation of fly ash composition to CaO · Al_2O_3 · SiO_2 ternary oxide systems.

Figure 16—Highest Strength Slags (50% CaO)

The composition of twenty fly ashes is plotted in Figure 16. The highest CaO content are for sources identified as M-6535, M6979 and M7124. These fly ashes plot near the edge of potential slag composition. As discussed earlier, the increase in CaO of fly ash increases the reactivity for strength potential.

In Figure 16, the lowest CaO content for slag is approximately 33% and the highest is 50%. Considering only three oxides are plotted, the numbers would each be reduced as these three oxides do not make up the complete composition. The approximations of 33% and 50% are slightly reduced from those shown in the figure.

Consider three Grades of slag 80, 100, and 120 of slag ground to the same fineness. If Grade 80 slag contains 33% CaO and Grade 120 contains 50% CaO, the CaO content of the Grade 100 slag is estimated as follows: For the Grade 80 (33 ÷ 0.80) = 41.7% for Grade 100 slag; and (41.7×1.2) = 50% for the Grade 120 slag. This calculation suggests that Grade 100 slag produces the same strength as cement, containing 41.7% CaO. This is the value used in this model.

There may be those who challenge the comparison of slag chemistry to fly ash chemistry. Slag is a glassy product as is the reactive portions of fly ash. It was demonstrated earlier and shown in in Figures 13 and 14 that fly ash CaO content relates directly to concrete strength. Increasing CaO in fly ash results in higher strength in concrete. This is also true of slag. Figure 16 points out that as the CaO content of slag increases, strength of concrete increases.

A concrete mixture made with 100% fly ash with 28.6% CaO resulted in a strength at one year equivalent to 70% of that produced by cement[7]. Consider (0.286÷0.417) = 68.7%, which is approximately 70%. In this model the value of 41.7% CaO approximates a Grade 100 slag and is used to calculate the self-cementing portion of fly ash. The value (41.7%) is confirmed by evaluating data on durability using the following assumptions.

The assumption is that "if" the degree of fly ash pozzolanic reaction is equal to the degree of the self-cementing reaction (based on the CaO content), the durability benefit using fly ash should be similar to or equal to the cement it is used with. This assumes that the degree of the self-cementing fly ash reaction is 50%.

The following calculations are used to estimate the self-cementing reaction for the von Fay ashes based on their CaO contents (10.9÷41.7) = 26.2%; (21.1÷41.7) = 50.6%; and (28.6÷41.7) = 68.7%. The second ash (#2 in Table 15 with CaO = 21.1%) is estimated to have self-cementing reaction of approximately 50% and the pozzolanic reaction is approximately 50%.

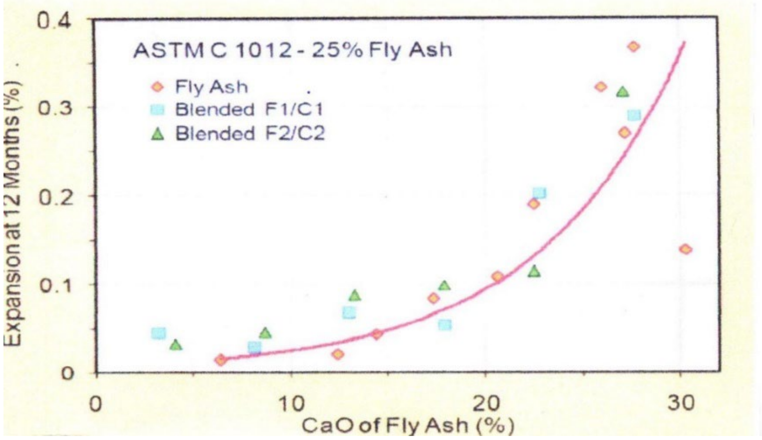


Figure 17—ASTM C 1012 Fly Ash CaO% Versus Sulfate Expansion[26]

Relationship between the 1-year expansion of mortar bars with 25% fly ash stored in 5%-Na_2SO_4 solution and the calcium content of the fly ash (Shashiprakash and Thomas 2001)[26]

Consider the data in Figure 17. The sulfate resistance expansion limit for ASTM C1012 is 0.1% at one year. In Figure 17, this expansion limit corresponds to fly ash CaO content of approximately 21% - it is assumed that a fly ash with this composition will have an estimated self-cementing reaction and a pozzolanic reaction at 50% each.

Sulfate resistance testing using an accelerated test on concrete was performed in the von Fay research using a failure criterion of expansion exceeding 0.50%. In Figure 18, expansion of concrete containing the fly ash with 21.1% CaO (identified as Low C) has a similar expansion as the control mixture with cement and no fly ash. he expansion of concrete with 10.9% CaO (Class F) ash was lower; and the mixture with 28.6% CaO (High C) fly ash had a very rapid expansion to failure.

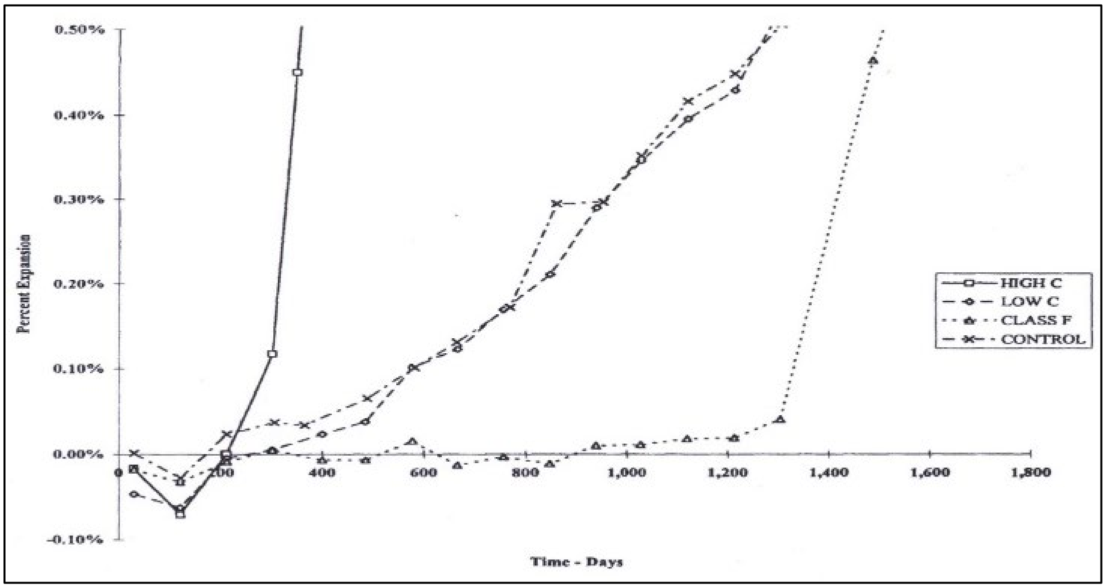


Figure 18—Figure 29 from von Fay USBR Concrete Accelerated Test (30% Ash)

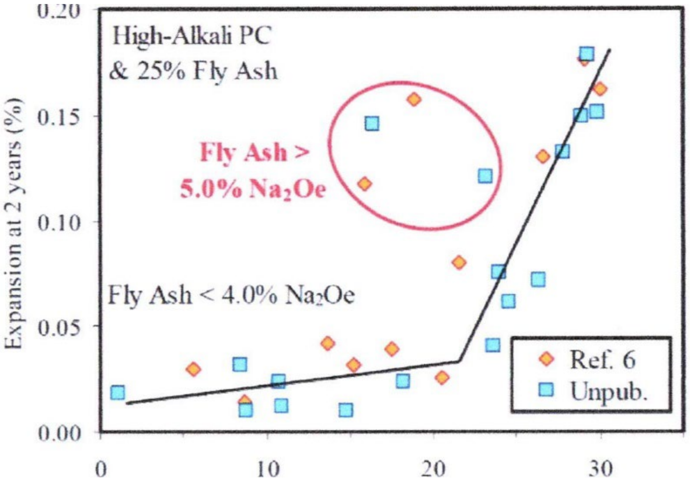


Figure 19—Fly Ash CaO% Versus ASR Expansion[27]

Relationship between the 2-year expansion of concrete prisms with reactive aggregate and 25% fly ash and the calcium content of the fly ash (Shehata & Thomas, 2002)[27]

The data for the effect of fly ash on mitigating alkali silica reaction (ASR) is shown in Figure 19 and illustrates that if fly ash CaO exceeds about 21% ASR expansion increases significantly.

Pozzolanic Reaction

In this model it is assumed that the pozzolanic reaction is when siliceous pozzolans react with calcium hydroxide. Reactions with aluminous phase in pozzolans will be briefly considered. The predominant hydration product of portland cement is calcium silicate hydrate (C-S-H) and the byproduct is lime or calcium hydroxide ($Ca(OH)_2$). It is assumed in this model that the reaction of pozzolan and lime produces the same hydration products as cement, C-S-H[28], by the following reaction:

$$3\,[Ca(OH)_2] + 2\,(SiO_2) = [3(CaO)\,2(SiO_2)\,3(H_2O)] \qquad \text{Eqn. 21}$$

Molecular reaction: 222 + 120 = 342

This balanced chemical equation shows that 222 parts of calcium hydroxide reacts with 120 parts of silica for a molar mass ratio of (222÷120) = 1.85. The value 1.85 is significantly higher than reported values. At 180-days Massazza[29] indicates values from 0.35 to 0.75. These reported values are based on the total mass of the pozzolan, which includes the reactive portion and the inert portion. If a pozzolan has 25% reactive and 75% inert that is non-pozzolanic and it combines with 46% of calcium hydroxide (0.25×222÷120), the reactive portion ratio is (0.46÷0.25) = 1.85, which agrees with molar mass ratio indicated by Eqn. 20.

Pozzolanic reactions could be between calcium hydroxide and aluminous phases in pozzolanic materials. In this case the final hydration product of aluminous compounds in cement is assumed to be $3(CaO).(Al_2O_3).6(H_2O)$, Consider the following pozzolanic reaction:

$$3[Ca(OH_2)] + Al_2O_3 + 3[H_2O] = 3(CaO)(Al_2O_3)6(H_2O) \qquad \text{Eqn. 22}$$

Molecular reaction: 222 + 102 + 54 = 378

The relationship between calcium hydroxide and alumina is (222 ÷ 102) = 2.18. Alumina combines with more calcium hydroxide than does silica.

The dominant strength producing reaction is between calcium hydroxide and silica. Therefore, the calculations that follow are based on silica only as the strength producing phase in the pozzolanic reaction. The portion of the strength due to alumina reactions is included as silica (a silica equivalent reaction).

Pozzolanic Index

In this model P_X is a pozzolanic index which has a value between 0 and 1. $P_{\%}$ is the pozzolan content as a decimal of total cementitious material. If at some later age, $P_X = 0.20$, 20% of the pozzolanic material will hydrate by reaction with calcium hydroxide. The remaining 80% is either self-cementing and non-reactive. If pozzolan content is 30%, $P_{\%}= 0.30$, there is 0.70 parts cement and 0.30 parts pozzolan. The amount of calcium hydroxide produced from 100% cement hydration is $(1.0 - 0.30) \times 0.25 = 0.175$ (17.5%). This is shown the topmost line of Figure 20 for $P_{\%}$ 30% with a Pozzolanic Index, $P_X = 0.00$, i.e., there is no pozzolanic reaction, so the calcium hydroxide content remains at 17.5%. For $P_X = 0.20$ (blue line in Figure 20), the amount of reacted calcium hydroxide is $(0.20\times0.30\times1.85) = 0.111$ and the non-reacted calcium hydroxide is $(0.175 - 0.111) = 0.064$ (the blue line in Figure 21). Note that filler effect is ignored, which would increase the hydration of cement and increase the amount of calcium hydroxide available, and thus it would be greater than 17.5%.

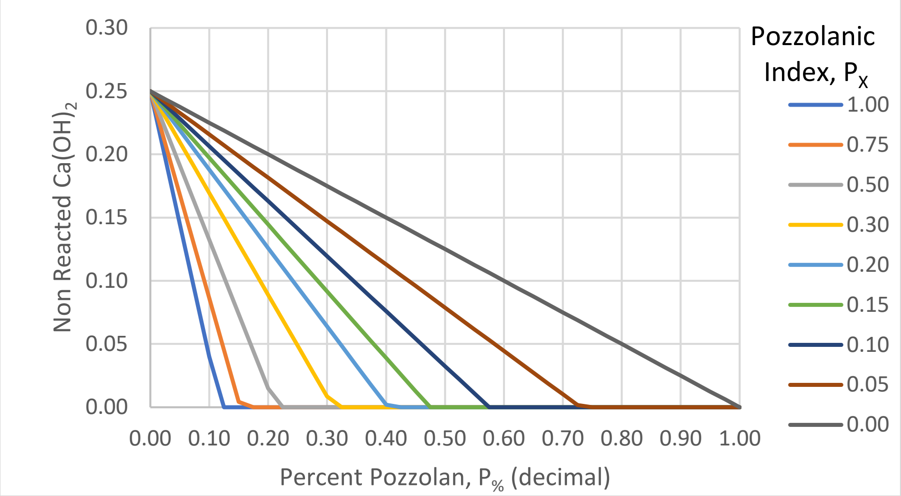


Figure 20—Non Reacted Lime Versus Percent Pozzolan

Consider Eqn. 23 below:

$$(1 - P_{\%}) \times 0.25 \div 1.85 = P_X \times P_{\%} \qquad \text{Eqn. 23}$$

The left side of Eqn. 23 calculates the amount of silica that can react with the calcium hydroxide available at $P_{\%}$. The right side of the equation is the amount of the pozzolan that is reactive, assumed to be reactive silica. Solving for P% produces the following:

$$P_{\%} = [0.25 \div 1.85] \div [P_X + (0.25\div1.85)] = 0.1351 \div (Px + 0.1351) \qquad \text{Eqn. 24}$$

If $P_X = 0.20$, $P_{\%}$ for Eqn. 24 is $[0.1351 \div (0.20 + 0.1351)] = 0.403$ (40.3%). In Figure 20 above (the blue line $P_X = 0.20$) the decimal percentage of pozzolan at which all the calcium hydroxide is consumed is 40.3% (non-reacted calcium hydroxide is 0). It is the highpoint for the blue line pozzolanic index = 0.20 ($P_X = 0.20$) in Figure 21.

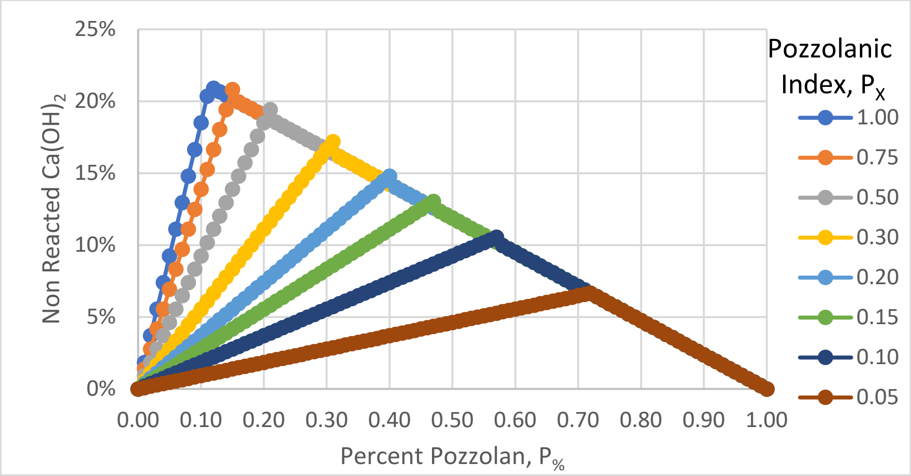


Figure 21—Non Reacted Calcium Hydroxide Versus Percent Pozzolan

Most Class F fly ashes at 28-days have a pozzolanic index less than 0.15; therefore the optimum fly ash content level to consume all the calcium hydroxide exceeds 40%. Using Eqn. 24 the optimum replacement for $P_X = 0.15$ is 47.4% and for $P_X = 0.10$ is 57.4%.

When the pozzolan percentage, $P_{\%}$, is greater than the optimum percentage (Opt) the degree to which that pozzolan reacts is based on the amount of calcium hydroxide available.

For $P_X = 0.20$ the following are applicable:

(1) If the pozzolan percentage exceeds the optimum amount, the pozzolan has the potential to react with all the calcium hydroxide. However, not all the reactive pozzolan will react because there is not enough calcium hydroxide in the system.
(2) If the pozzolan percentage is less than 40.3%, the reactive portion of the pozzolan can potentially react because there is excess calcium hydroxide in the system.

Theoretically, a perfect pozzolan is one that will result in 100% reaction with all the available calcium hydroxide, $P_X = 1.0$. The optimum content for this pozzolan based on Eqn. 24 is 0.1351 ÷ (1 + 0.1351) = 11.9% which is shown as the highpoint relative to the x-axis in Figure 21 for $P_X = 1$.

All data points in Figures 20 and 21 assume 100% reaction of cement. The ultimate hydration of cement is realistically less than 100% as calculated by Equation No. 7 and may have a modified H_{Index} due to WRA and/or the fly ash filler effect. The degree of ultimate hydration changes with w/c. The degree of hydration is less at early ages, such as 7 and 28-days. With a w/c of 0.50 the ultimate hydration based on Equation No. 7 is 0.50 ÷ (0.50+0.17) = 0.746 (74.6%).
For the Ore[10] mixtures the degree of hydration at 28-day is 85.4% of ultimate or 0.854 × 0.746 = 0.6371.
The amount of calcium hydroxide is estimated to be 0.6271 × 0.25 = 0.159 (15.9%) of the cement.
For 100% reaction of pozzolan at 28-days, the optimum percentage would be
(0.159 ÷ 1.85) ÷ [(0.159 ÷ 1.85) + 1.0] = 0.0791 (7.91%).
If there is less cement reaction, the amount of lime available to react with a fly ash is less, so the optimum pozzolan percentage is less.

If the pozzolan has a $P_X = 0.20$ at 28-days, the optimum content is 29.6% at 28-days.
When PX = 0.05 at 28-days, the optimum content is 62.8%.
With filler effect the amount of calcium hydroxide generated will be higher, therefore, optimum content will be greater than 62.8%.

Figures 20 and 21 are illustrations based on 100% hydration of the cement and that only occurs at significantly later ages with high w/c and using high content of fly ash with $H_{Index} = 0$, which is far from normal. Cement will not fully hydrate. If the hydration is less than 100%, the optimum content of fly ash is a moving target based on w/c, the amount of fly ash, and the filler effect which changes cement hydration.

In summary, the optimum quantity of fly ash changes with:

1. test age;
2. w/c;
3. chemical admixture content;
4. pozzolanic index;
5. filler effect; and
6. the amount of CaO in the fly ash.

Based on equation Eqn. 21 the total weight (mass) of hydrated pozzolan is 342 parts and 120 parts pozzolan. The relationship between weight of hydrated product and pozzolan is (342 ÷ 120) = 2.85.

The fly ash cement equivalent (C_{EQ}) shown in Table 15:

$$C_{EQ} = C_{EQ\text{-}C} + C_{EQ\text{-}P} \qquad \text{Eqn. 25}$$

$C_{EQ\text{-}C}$ is the Cement Equivalent for the cementitious portion
$C_{EQ\text{-}P}$ is the Cement Equivalent for the pozzolanic portion

$$C_{EQ\text{-}P} = C_{EQ} - C_{EQ\text{-}C} \qquad \text{Eqn. 25A}$$

$$C_{EQ\text{-}C} = C_{EQ} \times P_{CaO} \div 0.417 \qquad \text{Eqn. 26}$$

P_{CaO} is the decimal fraction of CaO content in the fly ash the value 0.417 was discussed earlier.

The amount of fly ash that reacts as a pozzolan is the following:

$$P_P = C_{EQ\text{-}P} \div 2.85 \qquad \text{Eqn. 27}$$

P_P is the weight of the fly ash that reacts as pozzolan.

The amount of calcium hydroxide from cement hydration that reacts with the pozzolan portion is as follows:

$$Ca(OH)_2 = C_{EQ\text{-}P} - P_P \qquad \text{Eqn. 28}$$

The Pozzolanic Index is calculated by equation No. 27

$$P_X = P_P \div P_W \qquad \text{Eqn. 29}$$

Equations 25-29 calculations are illustrated as follows.

The C_{EQ} for fly ash #1 for the von Fay mixtures using 30% fly ash at 28-days is 0.5840 (Table 15).
The weight of fly ash in the mixture of 170 lbs/yd^3,
$C_{EQ} \times P_W = 0.5840 \times 170 = 99.3$ lbs.
The CaO of this fly ash is 10.9%.
Cement equivalent for the cement portion is (0.109 ÷ 0.4166) × 99.3 = 26.0 lbs.
The pozzolanic portion is 99.3 – 26.0 = 73.3 lbs.
The weight of fly ash that reacted as pozzolan is (73.3 ÷ 2.85) = 25.7 lbs.
The amount of lime from the cement that reacted with the pozzolan is 73.3 – 25.7 = 47.6 lbs.
The Pozzolanic Index, P_X, is (25.7 ÷ 170) = 0.151.
The total ash that reacts is (26.0 + 25.7) = 51.7 lbs.
The total reaction for this ash at 28-days is (51.7 ÷ 170) = 0.304.

The C_{EQ} for fly ash #2 for the von Fay mixtures using 30% fly ash at 28-days is 0.6773 (Table 15).
The weight of fly ash in the mixture of 170 lbs/yd^3.

$C_{EQ} \times P_W = 0.6773 \times 170 = 115.1$ lbs.
The CaO of this fly ash is 21.1%.
Cement equivalent for the cement portion is (0.211 ÷ 0.4166) × 115.1 = 58.3 lbs.
The pozzolanic portion is 115.1 – 58.3 = 56.8 lbs.
The weight of fly ash that reacted as pozzolan is (56.8 ÷ 2.85) = 19.9 lbs.
The amount of lime from the cement that reacted with the pozzolan is 56.8 – 19.9 = 36.9 lbs.

The Pozzolanic Index, P_X, is (19.9 ÷ 170) = 0.117.
The total ash that reacts is (58.3 + 19.9) = 78/2 lbs.
The total reaction for this fly ash at 28-days is (78.2 ÷ 170) = 0.460.

Using these illustrated calculations and similar calculations for other percentages of fly ash will it be possible to model effects on durability?
For fly ash #1 the pozzolanic reaction with 30% fly ash is (0.151 ÷ 0.304) = 49.7%.
For fly ash #2 the pozzolanic reaction with 30% fly ash is (0.117 ÷ 0.460) = 25.4%.
For fly ash #1 the reduction of calcium hydroxide (reaction with pozzolanic portion) is 47.58 lbs and for fly ash #2 is 36.88 lbs.
The author has modelled sulfate resistance provided by use of fly ash in previous papers[31,32]. Using this strength model, is the reduction in calcium hydroxide a "key" to modelling durability? Overall calcium hydroxide reduction is:

1. a reduction in the amount of cement, a 30% fly ash content reduces cement by 30% and thus reduces lime by 30%, and
2. a reduction which results from pozzolanic reaction as in the examples above.

Is the remaining calcium hydroxide in the system the "key" to modelling durability?

USING THE MODEL AND LIMITATIONS

An Excel spreadsheet has been developed to predict strength of mixtures using this model based on data developed from several specifically recommended trial batches. The spreadsheet includes four tabs:

- User Instructions – access to the user's guide (pdf)
- Trial Batches for user input;
- Strength Prediction; and
- Concrete Mixture Constants.

Trial Batches

Three sets of trial batches of concrete are required to *calibrate* the model for the specific materials used:

Set 1 — Mixtures with cement only; do not use chemical admixtures or SCMs.

Set 2 — Mixtures used in Set 1 with chemical admixture.

Set 3 — Mixtures used in Sets 1 and 2 with the addition of an SCM, such as fly ash.

The accuracy of the strength predictions by this model relies on the accuracy of the data generated from the trial batches. The following are important:

- Accurate weights of materials for the trial mixtures;
- Accurate moisture content of each aggregate used – absorption and total moisture before batching
- Accurate density (unit weight) for each batch mixed;
- If several batches will be mixed, a larger quantity of aggregate should be stockpiled and properly mixed before quantities are extracted and weighed for the batch; and
- A representative sample of the aggregate should be taken before each concrete mixture is made to determine the total moisture content of the aggregate. Accurate measurements of aggregate moisture and associated concrete mixing water content is critical for the model to accurately predict strength.

The size of the trial batch will depend upon the amount of concrete needed for the tests performed, and the number of cylinders cast. The required tests are slump, density (unit weight), and air content by the pressure method. The **density of fresh concrete is required** and the model will not use the data for any mixture if this is not input in the spreadsheet.

Concrete used to perform slump, density, or air content tests should not be used to cast cylinders. Before a trial batch is introduced, the mixer should be *buttered* by using a smaller batch mixture similar in proportions to the first batch that will be mixed. The *buttering* mixture is introduced into the mixer and mixed for a couple minutes and discharged so that the inside of the mixer is adequately coated with mortar. The mixer is now ready for the first trial batch and subsequent batches if they are made in reasonably quick order after the first. If there is going to be a long delay between subsequent trial batches, such as overnight, the mixer should be washed out and buttered again before the subsequent trial batches are mixed.

Trial Batch Quantities

On the "Trial Batches" tab of the Excel spreadsheet input the specific gravity of all the concrete materials in row 10.

Assume the following trial batch quantities in lb/yd^3:

Cement = 600
Mixing water = 300
SSD sand = 1135
SSD coarse aggregate = 1750
Total weight = 3785
Theoretical unit weight = 3785 ÷ 27 = 140.14 lbs/ft^3.

Every Trial Batch **must** include a Name of ID for the mixture input Mix Name/ID field. If this field is not filled, the calculations will not be performed.

Input the batch quantities in the appropriate locations in the spreadsheet. Batch quantities should be based on SSD aggregates and actual mixing water content after adjustment for aggregate moisture content. Record slump, air content measured by the pressure method, and density (unit weight). If the adjustments for moisture content have been done correctly and the air content is on target, and the batch quantities for the laboratory trial batch have been correctly determined, the measured density (unit weight) should be close to the theoretical unit weight.

To achieve this, it is critical that the moisture content of the aggregates is accurately measured. If aggregates used have a low absorption (<1.0%), the lab may consider using air-dry aggregates. This requires a large indoor space to spread out enough sand and aggregate for a period of time to dry to a stable moisture condition. Once a stable aggregate moisture content is achieved, the water content of all trial batches will be reasonably accurate. This procedure was used by the USBR laboratories in Denver. When aggregates are in an air-dry condition, the batch weight of water will be greater than the mix design mixing water content to account for the water that will be absorbed by the aggregates. With aggregates that have a higher absorption, prepare the aggregate in a moisture condition greater than SSD and make the appropriate adjustment to the weight of batch water.

All this extra effort is to ensure that the input on the concrete mixture proportions and w/cm is accurate to improve the accuracy of the prediction by the model. Once the model has been properly calibrated with the materials and the trial batches, it will be able to propose mixture proportions for target strength. For example, if the specified strength on a project is 4000 psi concrete mixture and the intent is to over-design by 1000 psi for a target strength of 5000 psi, the model will suggest the mixture proportions that will produce a target strength of 5000 psi at 28-days or other selected test age. The proposed mixture will vary based on the water reducing admixture dosage and the percent of SCM selected. The proposed mixture will also vary based on target air content.

Set 1 Mixtures

The first category Set 1 mixtures are entered in rows 11-20 in the "Trial Batches" spreadsheet tab. This permits 10 trial batches for this set. These mixtures are with cement only and should not contain water reducing admixtures or supplementary cementitious materials. Even though these are not typical mixtures used in practice, it is important to produce these mixtures to calibrate the model to the cement and aggregates used. Ensure that the rows are completed sequentially without leaving blank rows.

Trial batches for Set 2 and Set 3 concrete mixtures establish additional model *constants* for the water reducing admixture and supplementary cementitious materials used.

The recommendation for Set 1 is a minimum of five mixtures with varying w/c ratio that will average to 0.50. For example, the w/c ratios of 0.35, 0.45, 0.50, 0.55, and 0.65 will average to 0.50. The aggregate constants will be specific to the aggregates used, and if the average w/c is 0.50 these aggregate constants can be compared to other evaluations using different aggregates. A separate spreadsheet file should be used with different aggregates. The effect of air content on concrete strength is adequately addressed in the model based on the actual measured air content, thereby accurately achieving a target air content, such as 6.0% for all batches, is not necessary.

The five mixtures for Set 1, discussed above could be five non-air entrained mixtures or five air entrained mixtures or any combination of air entrained and non-air entrained mixtures. Set 1 mixtures are the most critical mixtures used to calibrate this strength prediction model. Preparing more mixtures, exceeding five, will improve the estimate of the model constants and improve its predictability. An ideal maximum number of Set 1 mixtures would 10 mixtures; five non-air entrained and five air-entrained mixtures. The average W/C ratio for the 10 mixtures should be 0.50.

The model uses the predicted volume of hydrated product to predict strength from these Set 1 mixtures. The model constants developed from the Set 1 mixtures will be unique or specific to the cement, sand, and coarse aggregate used in the mixtures.

Concrete Strengths (Ages)

The measured compressive strength at different ages are entered for each mixture in the same sheet and on the same row for each mixture. Fields are provided to record measured compressive strength at ages of 1, 3, 7, 14, 28, 56, 70, 90, 180, and 365 days. It is not required to test concrete for strength at all these ages. The user picks the ages for strength testing and makes the appropriate total number of cylinders. Accuracy of strength prediction is improved if three cylinders are tested at each test age, but two cylinders for each age is adequate. Record the average strength of the cylinders tested at the same age. If the user initially inputs the strengths for 3, 7, and 28-days, the model will develop preliminary estimates of the constants. If additional cylinders have been cast for testing at later ages, such as 90 and 365- days, these data can be added when available. The same test ages should be used for all of mixtures in this and subsequent sets.

The model can be used to propose mixture proportions to achieve strengths up to the maximum age tested (in the Strength Prediction tab). Or it can be used to predict strength of alternative mixture proportions to the maximum age tested (in the Strength Prediction tab). When planning the batches and its size, the different test ages and maximum age should be established. All cylinders to be tested at different ages should be prepared from the same concrete mixture.

Set 2 Mixtures

The second set of concrete mixtures contain water-reducing admixture(s). Input for Set 2 mixtures should be in rows 21 to 100. Each subset of mixtures with the same water-reducing admixture dosage should be entered in rows of 10, i.e. 21-30, 31-40, 41-50, 51-60, 61-70, 81-90, and 91-100. For the subset of mixtures in rows 21-30, use the most common dosage of water-reducing admixture, for example 5 oz/100 lb. cement (cwt). For example, if the most common dosage used is 5 oz/cwt, target a slightly higher dosage at around 5.05 oz/100 weight. The model will predict strengths for dosages of 5.0 oz/cwt. The model will show an error if a prediction is needed for water-reducing admixture dosage greater than 5.05 oz/cwt. Make concrete cylinders from these batches to be tested at the same ages as tested for the control mixtures in Set 1.

To improve the prediction accuracy for admixture dosage a second subset of mixtures with a different admixture dosage can be added in rows 31-40. The dosage can be lower than the commonly used dosage for mixtures in rows 21-30, which will improve the strength prediction for mixtures containing an admixture at dosage of 5 oz/cwt or lower. Alternatively or additionally, a higher target dosage, say 6.5 oz/cwt, could be used and prediction would work with water-reducing admixture dosages up to 6.5 oz/cwt.

In this model admixture dosage is based on the total weight of cement and supplementary cementitious material (which will only be used in Set 3 mixtures).

It is suggested, if possible, that a subset of mixtures in rows 21-30 or 31-40 etc. have an average w/c ratio of 0.50. However, this is not a strict requirement. It is also not essential to make 10 mixtures in each subset, but at least five is recommended.

If a user wishes to use a combination of two admixtures, the ratio of the dosage of the two admixtures should be fixed at say 50/50 or 75/25 for all mixtures in Set 2. A separate copy of the Excel file with the Set 1 mixtures included in rows 11-20 should be saved to input a different water reducing admixture or an admixture combination.

The space provided to input data for admixtures will likely not be needed. Space provided allows for seven dosage levels of water-reducing admixtures, one each for rows 21-30, 31-40, 41-50, 51-60, 61-70, 81-90, and 91-100. All these rows do not need to be filled in to establish the model constants for the admixture being used.

Set 3 Mixtures

The third set of concrete mixtures to be input in rows 101 – 200 should contain a supplementary cementitious material, such as fly ash or slag cement. Each subset in Set 3 should contain the same percentage of SCM by weight of cementitious material. Each subset with the same percentage of SCM should be input in sets of 10 rows: 101-110, 111-120, 121-130, 131-140, 141-150, 151-160, 161-170, 171-180, 181-190, and 191-200. Similar to concrete mixtures with water reducing admixture, the most common percentage of SCM should be input in rows 101-110, for example concrete mixtures with 20% fly ash. The user should target trial batches with quantity of SCM marginally greater than the target quantity, for example use 20.5% fly ash if the target quantity is 20%.

If a user wants to add use 50% SCM (use 50.5%) prepare these mixtures and input the data in rows 111-120. The model will calculate constants for SCMs for 0% replacement up to the maximum percentage used. In the first case the model determines a constant for 0 up to 20.5% (SCM mixtures in rows 101 – 110); in the second case for SCM content between 0% and 50.5%. Space is provided for 10 different percentages of SCM. For example, 10%, 20%, 30%, 40% SCM can be input in first four subset rows. If the user wishes to add percentages not previously used, for example 17%, these mixtures can be added in the next available spaces. It is recommended to prepare at least five mixtures for each percentage SCM for the model to accurately determine the SCM constant. These mixtures in Set 3 may or may not contain a water-reducing admixture. For the least variability with using a water-reducing admixture, use the same dosage per 100 weight of total cementitious for each of set of fly ash mixtures, if possible. If possible, for each group of mixtures the varied w/cm ratios used should average to 0.50.

For a different SCM or combinations of SCMs, such as slag cement and fly ash in the same mixture, save the file with the control mixtures in Sets 1 and 2 as a separate file to input the data for these mixtures. The ratio of the SCMs used in these combination mixtures should remain the same, such as 50/50 or 75/25 for the set of mixtures.

Changing Cement or Aggregate

Create a new model with a new file if a different cement or different set of aggregates is used.

Predicting Strength

The "Strength Prediction" tab can be used after information of Trial Batches has been input for all three sets of mixtures. There are two options:

Part 1: The user will first enter a mixture with the quantities of each material in Column "B" and the specific gravity of materials in Column "C". The user will suggest a chemical admixture dosage and percentage of SCM. The mix design and the WRA dosage and SCM contents should be within the range used for the trial batch mixtures for calibrating the model. The model will predict the strength for the mixture entered in Row 22.

Part 2: The user can enter a strength level in Row 28 and the model will suggest mixture proportions to produce that strength using the same coarse aggregate content, water-reducing admixture dosage, SCM percentage, and air content as input in Part 1. The fields in Part 1 have to be input for Part 2 to work.

Caveat

Strength Predictions are based on the accuracy of mixture proportions used and of strength data generated from the trial batches. Errors in a trial batch, even small ones like a small change in air content will result in a small prediction error. Prediction error increases with each material added. For example, the prediction error increases with an increase in entrained air, addition of an admixture, or with the addition of an SCM. The goal is to minimize the error in each trial batch. Increasing the number of trial batches will improve the prediction and decrease the prediction error resulting from an error in single trial batch for a set of materials.

The predictions in this model are based on trial batches made at laboratory temperatures and for standard cured strength test specimens cured in the laboratory. If specimens cured in the field is higher than lab temperature, the 28-day strengths will be lower, and vice versa. The author has data demonstrating why and how temperature changes strength; however, these changes are not included in this model.

Concrete Mixture Constants

The tab "Concrete Mixture Constants" in the spreadsheets reveal the constants generated for the cement only mixtures; for the mixtures with water-reducing admixtures; and for the mixtures with SCMs. These constants can be compared with constants generated by using different cements or aggregates at different locations by the same producer.

Mixture Proportions and Strength Data Spreadsheet

A separate spreadsheet is provided for calculating trial batch quantities and strength data. These data can be copied into the Concrete Strength Model spreadsheet.

The Batch Calculations tab performs two functions:

The mixture proportions based on SSD aggregate for 1 cubic yard are input into Part 1. When ready to prepare trial batches, measure the moisture content (and absorption) of the aggregates and input the size of the trial batch in cubic feet. The spreadsheet will provide the batch quantities for the trial batches based on wet aggregate weights.

Complete the trial batch and perform the fresh concrete tests.

In Part 2, input the actual quantities used for the trial batch, the measured slump, unit weight, and air content. The spreadsheet will calculate the mixture proportions in lb/yd^3 on the basis of SSD aggregates. This information is captured at the bottom of the sheet and can be copied and pasted (**AS VALUES**) into the Concrete Strength Model spreadsheet for each trial batch performed.

Use a separate spreadsheet for each trial batch.

The Strength Data tab can be used to record the information when measuring strength at different ages. Input all the required data to calculate the strength of individual specimens and the average strength at each age. These data are captured at the bottom of the sheet and can be copied and pasted (AS VALUES) into the Concrete Strength Model spreadsheet for each trial batch performed. If strength was not measured at specific ages, delete any "zero values" pasted in the main spreadsheet.

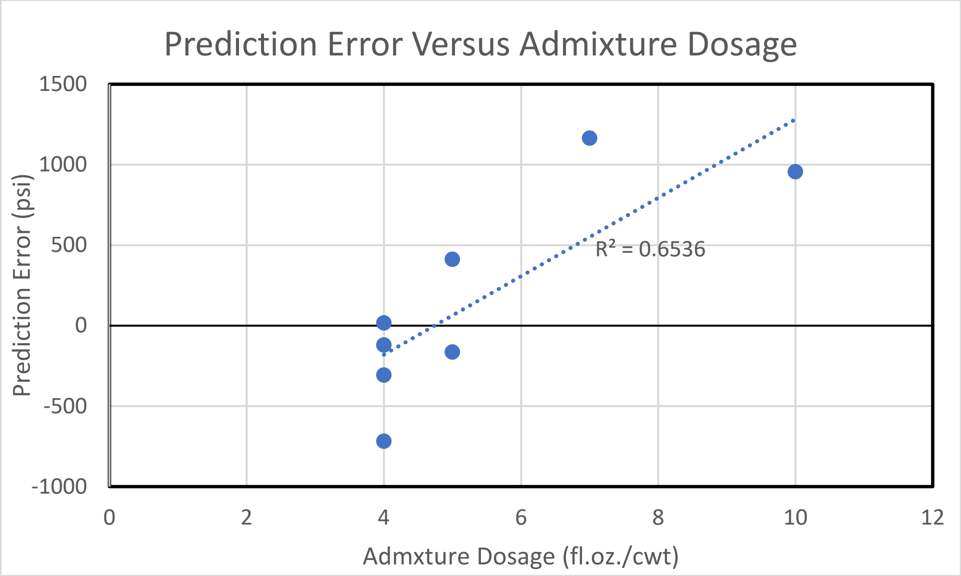
Use a separate spreadsheet for each trial batch.

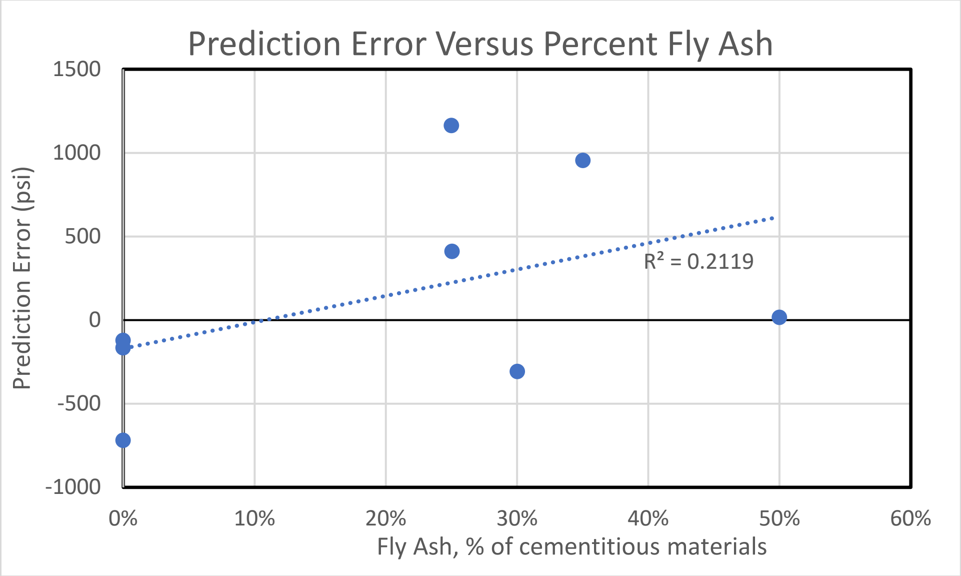
APPENDIX 1 – Additional Details and Considerations for Further Validation

Variable prediction errors of the strength model

As part of this concrete strength model study, several batches were made at the NRMCA laboratory to *calibrate* the model. These data are reported in Appendix 2, Tables A2-A, A2-B and A2-C for mixtures with cement only, cement with water reducing admixtures, and cement + fly ash with water reducing admixtures, respectively.

Eight concrete mixtures were made predict strengths based on the calibrated model. These are referred to as the *blind* concrete mixtures and the data and the predicted strengths are reported in Appendix 2, Table A2-D. The average prediction error for these 8 concrete mixtures (average error for strengths at 7, 28, and 70 days) in the two figures below:





For the NRMCA concrete mixtures with cement only, the predicted strengths were close to the measured strength. The prediction error is similar to other data sets in this report. In some cases, the prediction error is signifcantly higher. This is observed for concrete mixtures containing a water reducing admixture and/or fly ash. The average prediction error is the highest for concrete mixtures No. 23 (1164 psi) and 24 (955 psi) in Table A2-D. The admixture dosage appears to be the primary factor resulting in the higher prediction errors, primarily for admixture dosages of 7 and 10 fl.oz./cwt.

The hydration index values for the water reducing admixture calculated in the model were determined using three concrete mixtures, shown in Table A2-B. There are two control mixtures with an admixture dosage of 3 fl.oz./cwt and one control mixture with an admixture dosage of 6 fl.oz./cwt. There is no control mixture with an admixture dosage as high as 10 fl.oz./cwt. The hydration indices calculated in this report are shown in Figure 12.

If more control mixtures were made with a WR dosage of 3 fl.oz./cwt and some mixtures with a WR dosage of 10 fl.oz./cwt, a more accurate average hydration index at these dosage levels would have been available and most likely would have reduced the prediction error. If the average hydration indices are modestly increased, the prediction for cement hydration would be reduced and the fly ash C_{EQ} might increase to the same level as other Class F fly ash shown in Table 15.

In the section titled "USING THE MODEL AND LIMITATIONS" it is suggested that a minimum of five concrete mixtures should be made to calculate model constants for the specific materials used. If the hydration indicies are determined using at least 5 concrete mixtures each at 3 fl.oz./cwt and at an expected higher dosage of 10 fl.oz./cwt, the average value of hydration indices would be more representative of these concrete mixtures and will most likely reduce prediction error.

At the start of this research it was theorized that one control concrete mixture is needed to produce good strength predictions. This is proposed to only be true if hydration index for mixtures with water reducing admixtures is determined as the average for 5 or more concrete mixtures. This statement is also relevant: *However, even well controlled laboratory testing has variability; therefore, a single concrete mixture will not answer any of the questions discussed here.*

Does the model predict the strength when additional water is added at the plant or at the jobsite?

The model will predict strength with additional water added at the plant. Slump loss is real. If the project requires a 4-inch slump and slump loss is 2 in. during transit, is there strength loss if the slump is increased in the plant to 6 in. to arrive at the jobsite at a 4 in. slump? Based on the concrete mixtures from Ore, using a water content of 252 lb./yd^3 and a cement content of 552 lb./yd^3 the predicted strength was 5005 psi. Adding two gallons per cubic yard of water at the plant reduces strength only marginally to 4986 psi. The w/c ratio increases from 0.455 to 0.485 and increases the amount of cement that hydrates in accordance with Eqn. 7. The added volume of water, however, increases the yield which in turn reduces strength. With the increase in hydration and the increase in yield the net effect is a slight decrease in strength.

The model (Excel) does not predict the impact on strength with a jobsite addition of water. Water addition at the jobsite to increase slump is a bit different. The internal structure of the gel is established with initial mixing. Late addition of water does not change the internal structure; the prediction from Eqn. 7 values is not changed. Early addition of water in the plant increases the degree of hydration. Delayed addition of water at the jobsite does not increase the hydration. The addition of water increases the yield and simulates the impact on strength like an increase in air content. The decrease in strength is similar to the impact of increasing air content to decrease strength. A 2-gallon per yard water addition at the jobsite to increase slump by 2 in. results in a predicted strength of 4713 psi (a decrease of 292 psi, or 146 psi per inch of slump). It is suggested that the addition of water on the jobsite can be estimated by increasing the air content by the volume of the water added. For example, two gallons of water is 16.6 lbs which is $16.6/62.4 = 0.27$ ft^3 which is equal to a 1.0% increase in air content. This suggested impact on the strength predictions by this model needs additional validation. This evaluation should compare effect on strength with early addition of water to delayed addition to support these postulations.

Will the use of combined aggregate gradation increase strength?

The effects can go either way. If a combined aggregate gradation slightly increases water demand or if the quantity of cement is decreased by a small amount, the quantity of cement that hydrates is increased with a higher w/cm as predicted by Eqn. 7. This increase in hydration will in a small way offset the decrease in strength resulting from the decreased cement content. The increased hydration of cement is, however, more important than the quantity of cement in the mixture. Changing aggregate gradations can potentially change the aggregate constants calculated by this model, besides other factors, thereby changing the strength prediction.

Does the model work with slag cement, silica fume, natural and other pozzolans?

This model has been developed primarily with fly ash as the supplementary cementitious material. Further validation is needed with other SCMs and with ternary blends of cementitious materials.

Can the model be used to characterize different concrete aggregates?

It may be possible to develop constants associated with aggregate-to-cement bond and aggregate strength. These constants may make it possible to characterize how different aggregates perform in concrete mixtures. This would entail a considerable evaluation of different aggregate types.

What are the unique aspects of this model for strength prediction?

These are some of the unique features of this model:

- Eqn. 7 is an important development in this model to predict strength;
- The method to determine the effect of air content on strength;
- The method of obtaining a constant for WRA;
- The method of considering the filler effect;
- The evaluation of the impact of initial temperature on strength of concrete; and
- Separating self-cementing and pozzolanic reaction for fly ashes.

Can this model be extended to evaluate the durability of concrete mixtures, such as sulfate resistance and ASR?

This model separates the self-cementing and pozzolanic reactions of fly ash that could be used to model durability. Additional evaluation and validation would be needed to model durability. Durability has been modeled by the author[31, 32]. Strength data from von Fay[7] has been used extensively in the development of this model. This research included long-term testing of concrete for sulfate resistance, freeze-thaw durability, and heat of hydration. Durability testing was performed on the same concrete mixtures that were tested for compressive strength. The hydration calculations in this model to predict durability that needs to be validated by durability tests. The EPRI research[6], Regions 1 to 5, also include durability testing for sulfate resistance, freeze-thaw durability, and includes other performance data such as setting time, shrinkage, flexural strength, and modulus of elasticity.

Can a petrographic examination determine w/c ratio?

A petrographer retains reference samples of known w/c ratio to compare with the test sample. Suprenant and Malisch[33] observe that *Petrographers typically have prepared samples of concrete with varying water-cement ratios for use as comparison samples*. The amount of unhydrated cement in concrete is

inversely related to water-cement ratio. (Eqn. 7 and Figure 2).
Based on Eqn.7 the ultimate amount of cement hydration at a water-cement ratio of 0.40 is
$0.40 \div (0.40 + 0.17) = 0.701$ (70.1%), and
the ultimate hydration for a water-cement ratio of 0.61 is
$0.61 \div (0.61 + 0.17) = 0.782$ (78.2%).
The unhydrated cement is 29.9% and 21.8%, respectively and the difference is 8.1%.
Suprenant and Malisch[33] point out that the difference in unhydrated cement identified by petrographers between these two water-cement ratios is approximately 8%. However, a petrographer suggests that there is little-to-no unhydrated cement remaining in concrete with a w/c ratio of 0.61 and approximately 8% unhydrated cement in concrete with a w/c ratio of 0.40. Suprenant and Malisch[33] point out that *the unhydrated portland cement of the concrete may appear to have a water-cement ratio of about 0.40 when in fact it was made at a ratio of 0.60 or higher*. They point out the curing temperature can influence the amount of unhydrated cement (See Table 13). If cooler concrete temperature modifies H_{Index}, it will change the degree of hydration and thus the amount of unhydrated cement.
If a cooler temperature changes H_{Index} from 0.17 to 0.11, the degree of hydration at a w/c ratio of 0.40 is $0.40 \div (0.40 + 0.11) = 0.784$ (78.4%). The amount of unhydrated cement is 21.6% and the petrographer reports a water-cement ratio of 0.60 when the real water-cement ratio is 0.40.

Eqn. 7 predicts the hydration based on research by Mills[14]. As discussed earlier, in this research samples of cement and water were placed in sealed bottles and rotated with marbles to expose as much cement as possible to water and hydration. Even under these conditions a high percentage of cement had not hydrated. Mills[14] and Powers[4] determined the degree of hydration by heating oven-dried hydrated paste to a high temperature to remove the water bound in the hydrated products. This "loss on ignition" is used as a measure of the degree of hydration. Petrographic visual observations essentially view particles where the hydrated cement encapsulate the unhydrated cement that cannot be quantified. Petrographic observations are thereby not in sync with estimated hydration reported by Mills, Powers, and others. The degree of hydration reported by them is much lower than that seen in the reference samples of concrete with different w/c ratio used by petrographers.

Richardson, et al.[34] discusses observations of hydrated cement at a microscopic level using a scanning electron microscope. They observed that the hydration product Calcium Silica Hydrate (C-S-H) has an "inner" and "outer" layer and the composition of hydrates in these layers are different. The Ca/Si ratio in the "inner" product is higher than that in the "outer" layer. Calcium hydroxide (lime) is mainly confined to the "outer" layer. If the inner product lacks in calcium hydroxide, can it be considered un-hydrated cement? Inner product is only observed in high magnification scanning electron microscopes and will not be observed in optical microscopes used by petrographers.

What is the intrinsic strength of a cement?

To avoid rounding in calculations, this section shows 6 significant figures from values in Excel spreadsheet. The calculated intrinsic strength is indicated to 6 significant figures in the numerical values.

In this discussion intrinsic strength is the strength of a completely hydrated cement paste that completely fills a specific volume of 1. The volume includes only hydrated cement (C-S-H strength producing gel) and does not include the volume of calcium hydroxide and gel water.

Earlier in this report it was assumed that 1 gram of portland cement requires 0.243243 grams of water for complete hydration.
The volume of 1 gram of cement = $1 \div 3.150000 = 0.317460$ cm^3.
Powers[4] states: *The hydration of one cubic centimeter of portland cement produces about 2.06 cm^3 of gel*

plus the non-gel constituents.
The volume of 1 gram of hydrated cement paste = (2.06000 × 0.317460) = 0.653968 cm^3.

Powers[4] also states: *The density of the nominal gel is about 2.15 g/cm^3, its porosity is about 26%....*
The following calculations are based on a porosity of 26.2867%.
The solid volume = (1 - 0.262867) × 0.653968 = 0.482062.
Volume of gel water volume = 0.653968 – 0.482062 = 0.171096 (0.17 was estimated with Eqn. 7).
Original volume of cement and water = 0.317460 + 0.243243 = 0.560704.
Hydration increased the volume by (0.653968 ÷ 0.560704) = 16.6335%

Total mass = 1 g (cement) + 0.243243 g (water) + 0.171096 g (gel water) = 1.419593 g.
The saturated density = (1.419593 ÷ 0.653968) = 2.156083; consistent with Powers' value of 2.15.

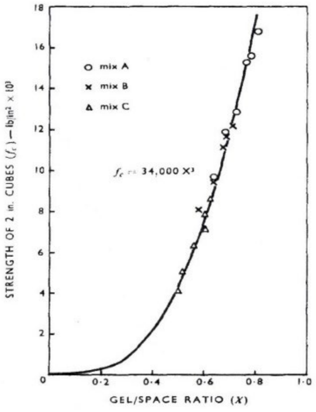
If the gel porosity that is filled with water is instead filled with hydrated cement, there is an increase in solid volume of hydrated cement.
Volume of hydrated cement is estimated = (0.171096 ÷ 0.482062) = 0.356607
This is a 35.6607% increase in hydrated cement.

Powers[4] also states: *The gel substance proper, corrected for calcium hydroxide, has an average density of 2.65 g/cm^3.*
It is assumed that hydration of portland cement produces 75% C-S-H (hydrated product that contributes to strength) and 25% calcium hydroxide. The density of C-S-H is 2.65 and the density of calcium hydroxide is 2.24.
The total original mass determined earlier is 1.419593.
Volume of C-S-H = (0.75 × 1.419593) ÷ 2.65 = 0.401771
Volume of calcium hydroxide = (0.25 × 1.419593) ÷ 2.24 = 0.158437
Total volume = 0.560208.
Volume of C-S-H contributing to strength = (0.401771 ÷ 0.560208) = 0.717182.

The hydration reaction of cement and water (0.560704) results in a reduction in volume of the reacting materials to produce a volume of solids = 0.482062.
The hydrated solid volume = 0.482062 ÷ 0.560704 = 0.859744.
The volume of C-S-H contributing to strength = 0.717182
The reduction in volume of solids by hydration = (0.859744 × 0.717182) = 0.616593.

If the gel porosity is filled with hydrated C-S-H, the volume of C-S-H increases by 35.6607%
The volume of C-S-H including that in the gel porosity = 1.356607 × 0.616593 = 0.836475.
Normalizing this solid volume to 1 = (1 ÷ 0.836475) = 1.195493
Total volume of C-S-H is increased by 19.5493%.
The total increase in C-S-H = 1.356607 × 1.195493 = 1.621814.

It was demonstrated that strength is related to the volume of hydrated cement raised to the third power and illustrated in Figure 1 (also below).
The total volume raised to the third power: 1.6218143 = 4.265828.



Powers estimated that the compressive strength for a fully hydrated cement is 34,000 psi. This includes the C-S-H with gel water volume and calcium hydroxide. Using the concepts above, if all this volume is completely hydrated C-S-H, would the intrinsic strength = 4.265828 × 34,000 =145,038 psi?

Consider the work by Roy and Gouda[13]. They hydrated cement pastes with low water cement ratios and at high temperatures and under high pressures. This method produced a cement paste with both hydrated cement and calcium hydroxide with very low porosity with compressive strength exceeding 80,000 psi and in one case 94,600 psi. These pastes were not fully hydrated and had estimated degrees of hydration between 29 and 37%. The hydrated C-S-H in this discussion contains only fully hydrated cement with no calcium hydroxide and would have strengths significantly greater than those of Roy and Gouda.

In SI units an intrinsic strength of 145,038 psi is 1000 MPa.

The "constants" used above will vary with the cement characteristics. About half of the water in the gel porosity is related to chemical shrinkage, which is the reduced volume due to the hydration reaction. The remainder of the volume of water in the gel porosity is likely due to the physical gradation of the cement particles which create voids in the cement paste. The physical constants suggested by Powers[4] are 2.06 and 0.26 and they are directly related.

Using 1000 MPa as the intrinsic strength there are other combinations of these two constants that will give the same intrinsic strength. In the above example the constants 2.06 and 0.262867 were used. Other combinations include (2.056 and 0.261432), (2.055 and 0.261074), (2.054 and 0.260713), and (2.052 and 0.2600). These combinations of constants all produce the same intrinsic strength. As the constant 2.06 is decreased the porosity decreases and as 2.06 is increased to 2.064, for example, the porosity estimate increases to 0.264292. These two constants are physical constants rather than chemical and they are indicators of porosity in that an increase in either constant results in an increase in porosity.

Caveats

What are the real numbers rather than *about 2.06* or *about 26%* porosity? Powers[4] wrote that the value of 26% comes from the assumption that hydrated cement particles are spherical and when stacked together result in the lowest porosity of 26%. The following is a quote from Powers[4]: *gel porosity is about 26%, for spheres, requires a packing like stacked cannon balls*. Powers admits that cement particles are not spherical like cannon balls, and in later work Powers[35] suggested that the porosity is about 28%. Mindess et.al.[16] suggested that 2.06 should be 2.10 and that the volume of gel water is 0.14 rather than 0.17. Is 34,000 psi suggested by Powers[4] the exact number he found in his analysis? There is some indication in his early work that it might be 34,200 psi and that value was used in previous modelling by Dunstan[6] and that value is included in an equation by Neville[15]. This section suggests that cement has an intrinsic strength of 1000 MPa. This depends on the cement chemistry, its particle size distribution, its particle shape, and the assumption that the water content for 100% hydration is 0.243243. As these assumptions change, the intrinsic strength will vary to some degree from 1000 MPa.

Powers[4] considered the intrinsic strength to be the strength of 100% hydrated portland cement with water filled space and hydrated lime. However, the intrinsic strength discussed in this section can be the result of many different reactions. Modern concrete mixtures contain chemical admixtures and commonly supplementary cementitious materials such as fly ash, slag cement, silica fume, natural pozzolans, and other materials It is pointed out in this report that water reducing admixtures increase the hydration of cement directly proportional to the dosage of the admixture used. Supplementary cementitious materials such as fly ash are fillers and increase the hydration of cement. Future research can define the magnitude of filler-induced hydration. Some of the additional questions that can be answered:
Some of these SCMs through the pozzolanic reaction, react with hydrated lime from the cement hydration to form strength producing C-S-H and fill some of the space occupied by the hydrated lime. What is the optimum amount of pozzolanic material? What is a perfect pozzolan?
Some of these materials, like slag cement and Class C fly ash, produce C-S-H by self-cementing reactions. What is the magnitude of each of these self-cementing reactions?
How much of each of these materials are inert and should be considered as fine aggregate?
The intrinsic strength suggested in this report results from a C-S-H product that completely fills the available volume and could be produced by any of these chemical reactions. Therefore, the source of the strength producing C-S-H may be from the cement, or from a pozzolanic reaction from Class F fly ash or other pozzolans, or from self-cementing reactions.
Can a perfect concrete mixture be designed with just the right amount of each material to fill the total available volume with C-S-H by consuming all the calcium hydroxide and filling all the water filled space?
It is almost impossible to design a concrete mixture that is “workable” and contains the correct combination of materials to produce the required amount of hydration products to fill all the available space. Strength of currently made concrete mixtures is no longer due to cement hydration only and this makes it difficult to estimate the intrinsic strength. If 100% of the available volume is filled with strength producing C-S-H from various reactions is the intrinsic strength still 1000 MPa?

In conclusion, this report demonstrates that the easiest test to perform-compressive strength, can be used to predict the level of hydration (the key). However, even well controlled laboratory testing has variability; therefore, a single concrete mixture will not answer any of the questions discussed here.

APPENDIX 2 – Mixtures at the NRMCA Research Laboratory

Table A2-A – Control Concrete Mixtures – Cement only						
	Mixture No.**					
	5	6	7	11	12	13
Mixture Proportions						
Cement, lb/yd^3	889	517	680	642	843	471
Fly Ash, lb/yd^3	0	0	0	0	0	0
Water, lb/yd^3	349	336	333	308	335	298
Sand, lb/yd^3	1071	1372	1254	1164	1001	1281
Coarse Aggregate, lb/yd^3	1919	1907	1927	1922	1953	1885
WRA, fl.oz./cwt	0	0	0	0	0	0
AEA, fl.oz./cwt	0	0	0	1	1.3	0.90
w/c	0.393	0.650	0.490	0.480	0.397	0.633
Fresh Concrete Properties						
Measured Air, % (C231)	1.4	1.9	1.5	5.8	3.5	7.9
Grav. Air, % (C138)	0.4	1.6	1.0	5.3	3.0	7.2
Density, lbs/ft^3 (C138)	156.6	153.0	155.3	149.5	153.1	145.8
Slump, in. (C143)	4.75	6.75	6.50	7.50	5.25	7.50
Measured Strength, psi						
7-day	5627	3404	4692	4123	5138	2700
28-day	7184	4964	6493	5158	5928	3881
70-day	7602	5293	6894	5700	6656	4147
Predicted Strength, psi						
7-Days	5730	3487	4597	3940	5186	2755
28-Days	7002	4983	5983	5164	6378	4033
70-Days	7620	5340	6469	5579	6935	4313
**Mixtures 1-4 were used to establish procedures, therefore test results for these mixtures are not reported.						

Table A2-B – Mixtures with Cement and WRA			
	Mixture No.**		
	8	**9**	**10**
Mixture Proportions			
Cement, lb/yd^3	619	801	476
Fly Ash, lb/yd^3	0	0	0
Water, lb/yd^3	310	319	302
Sand, lb/yd^3	1342	1207	1460
Coarse Aggregate, lb/yd^3	1897	1915	1896
WRA, fl.oz./cwt	3.0	6.0	3.0
AEA, fl.oz./cwt	0	0	0
w/c	0.500	0.398	0.634
Fresh Concrete Properties			
Measured Air, % (C231)	2.1	1.4	2.8
Grav. Air, % (C138)	2.1	0.8	2.6
Density, lbs/ft^3 (C138)	154.4	157.1	153.2
Slump, in. (C143)	5.00	7.00	3.50
Measured Strength, psi			
7-day	4937	5958	3193
28-day	6426	8002	4679
70-day	6997	8620	5100
Predicted Strength, psi			
7-Days	4663	7058	3474
28-Days	6035	8170	4975
70-Days	6552	8943	5353

Table A2-C – Mixtures with Cement, Fly Ash, and WRA						
	Mixture No.**					
	14	**15**	**16**	**17**	**18**	**19**
Mixture Proportions						
Cement, lb/yd^3	480	624	367	341	172	616
Fly Ash, lb/yd^3	120	156	92	228	401	154
Water, lb/yd^3	300	304	288	285	287	309
Sand, lb/yd^3	1360	1231	1475	1353	1372	1215
Coarse Aggregate, lb/yd^3	1900	1928	1890	1864	1911	1903
WRA, fl.oz./cwt	3.0	8.0	3.0	3.0	1.13	4.80
AEA, fl.oz./cwt	0	0	0	0	0	0
w/cm	0.500	0.390	0.627	0.50	0.500	0.401
Fresh Concrete Properties						
Measured Air, % (C231)	2.2	1.3	2.9	4.2	2.0	1.6
Grav. Air, % (C138)	2.0	0.6	3.1	3.9	1.4	1.4
Density, lbs/ft^3 (C138)	154.1	157.2	152.3	150.8	153.5	155.4
Slump, in. (C143)	6.75	8.50	4.50	7.50	4.75	7.50
Measured Strength, psi						
7-day	2722	5265	2255	2161	687	4731
28-day	4807	7004	3550	3662	1124	6609
70-day	6067	8156	4367	4870	1754	7977
Predicted Strength, psi						
7-Days	3265	5418	2054	906	687	4683
28-Days	5057	7012	3928	2965	1124	6330
70-Days	6154	8324	4846	3391	1754	7597

Table A2-D – Concrete Mixtures – Blind Measured Strength (to predict)

	Mixture No.							
	20	**21**	**22**	**23**	**24**	**25**	**26**	**27**
Mixture Proportions								
Cement, lb/yd^3	560	647	452	498	527	566	244	289
Fly Ash, lb/yd^3	0	0	151	166	284	0	244	124
Water, lb/yd^3	297	297	265	270	281	301	241	248
Sand, lb/yd^3	1400	1298	1267	1317	1134	1385	1338	1411
Coarse Agg., lb/yd^3	1880	1966	1901	1967	1973	1899	1855	1866
WRA, fl.oz./cwt	4.0	5.0	5.0	7.0	10.0	4.00	4.00	4.00
AEA, fl.oz./cwt	0	1.20	1.80	2.00	4.00	0	0.90	0.40
w/cm	0.530	0.459	0.439	0.410	0.346	0.531	0.495	0.600
Fresh Concrete Properties								
Measured Air, % (C231)	0.60	2.7	6.6	1.7	2.9	2.4	9.4	7.7
Grav. Air, % (C138)	3.1	2.0	6.0	2.0	2.0	2.7	8.4	8.2
Density, lbs/ft^3 (C138)	153.2	155.9	149.5	156.2	155.5	153.7	145.3	145.8
Slump, in. (C143)	2.75	5.25	7.75	8.25	8.25	6.75	8.00	4.50
Measured Strength, psi								
7-day	4,356	5,276	3,400	4,506	4,736	3,937	1,230	1,338
28-day	5,681	6,861	4,915	6,786	7,211	4,879	2,029	2,114
70-day	6,104	7,032	6,021	8,108	9,006	5,817	3,064	3,108
Predicted Strength, psi								
7-Days	4445	5519	2964	3742	4562	4532	987	1109
28-Days	5781	6771	4532	5461	6035	5880	2156	2746
70-Days	6266	7373	5604	6705	7489	6374	3127	3626

APPENDIX 3 – Sources of Fly Ash

Number	Utility	Plant	Coal Source
#1	Salt River Project	Navajo	Arizona
#2	Arkansas Power and Light	White Bluffs	Wyoming
#3	Public Service Co. of Colorado	Pawnee	Wyoming
#4	Pennsylvania Power and Light	Montour	Pennsylvania
#5	Pennsylvania Electric Co.	Conemaugh	Pennsylvania
#6	Pennsylvania Power Co.	Bruce Mansfield	Ohio
#7	East Kentucky Power Co.	John Sherman Cooper	Eastern Kentucky
#8	Louisville Gas and Electric Co.	Mill Creek	Western Kentucky
#9	Alabama Electric Cooperative	Tombigbee	Alabama
#10	United Power Association	Coal Creek	North Dakota
#11	Wisconsin Power and Light Co.	Columbia	Montana
#12	Illinois Power Company	Baldwin	Illinois
#13	Wisconsin Electric Power Co.	Pleasant Prairie	Wyoming
#14	Public Service Co, of Colorado	Cherokee	Colorado
#15	Basin Electric Power Cooperative	Laramie River	Wyoming
#16	Kansas City Power and Light Co.	Montrose	Missouri and Oklahoma
#17	Unknown—Lab Ash---NRMCA		

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