In House Research

NDOR Research Section

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Blended Cement Chemical Evaluation (Oxides) for NDOR Quality Assurance

Nebraska Department of Roads

Research Project Title:
Blended Cement Chemical Evaluation (Oxides) for NDOR Quality Control

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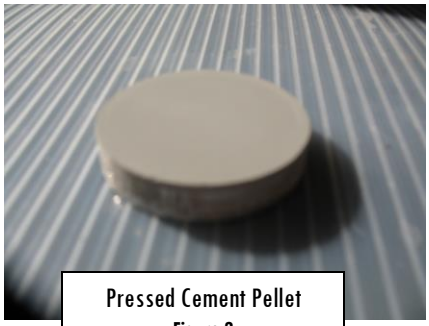
Purpose of the Research Project:
NDOR currently requires use of IPF cement which is a binary cement pre-blended to contain both Type I/II cement and 25% Class F Fly Ash, for use on all concrete applications. Previous research showed that the aggregate found in Nebraska is highly reactive and causes severe concrete deterioration unless 25% of the Class F Fly ash is included.
Therefore, the purpose of this study was undertaken to investigate the possibility to determine a quality assurance process for NDOR to verify the percentage of supplementary cementitious materials (SCM) required in blended cements for the compliance of its use in Nebraska state highway construction.
The objective of this project was to find the effectiveness of using X-Ray Fluorescence (XRF) Spectroscopy shown in Figure 1 for quality assurance of blended cements. XRF is currently used to chemically analyze cement and SCM's by pressing the material into a pellet shown in Figure 2. The project scope was based in two phases and an implementation plan as follows:

Description of Research Project:

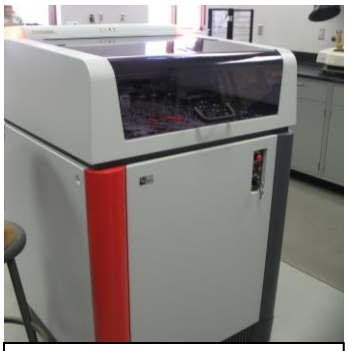
Phase 1:

Purpose:

- To develop a correlation between NDOR and suppliers from the XRF results with the common chemical requirements found in fly ashes such as: silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), and calcium oxide (CaO).
- To verify NDOR specifications for the total percent required of SCM in blended cements.



Pressed Cement Pellet
Figure 2



X-Ray Fluorescence Spectrometer
Figure 1

Steps of Lab Correlation Analysis:

1. NDOR sent 10 samples of blended cement (1PF) to the three current suppliers for the State of Nebraska (Holcim, Ash Grove, and Lafarge) for XRF analysis testing within their laboratories.

2. Each supplier provided NDOR with their own equation to calculate the percentage of Class F Fly Ash in the blended cements, which they used for their own quality assurance.

3. NDOR compiled and analyzed all XRF chemical analysis results from within the three suppliers. The percent amount of Class F Fly Ash in the blended cement was determined using suppliers' equations. A correlation factor was developed to compare percentage of Class F Fly Ash in blended cements between the suppliers and NDOR.

Summary of Phase 1:
The results of Phase 1 have shown an inconsistency from the XRF chemical analysis results between NDOR and suppliers. Therefore, NDOR could not develop a standard method for a quality assurance testing program. Due to the findings in Phase 1, NDOR started looking at the mechanistic reaction between Hydraulics (Cement) and Pozzolanic (Ashes) reaction. One of the first steps was to go back to the basics of understanding the process between the Pozzolanic reactions, where a pozzolan is used as a partial cement replacement to help reduce and prevent the Alkali-Silica Reaction (ASR). It is known and believed that the reaction of Calcium Silicate with Calcium Hydroxide is what will provide the strength and permeability of concrete.

As a result of the relationship of the calcium silicate hydrate (C-S-H) between cement and SCM, NDOR started to look at the relationship of calcium and silica because it's known to benefit the prevention of ASR. However, the ratios of other chemical oxides were also considered to review all possibilities within different ratio combinations. Therefore, the beginning of Phase II took place as follows:

Phase 2:

Purpose:

- To analyze a pattern between the ASR results and the data from different ratio combinations of the relevant oxide contents of the blended cements. ASR results were obtained by the standard method of ASTM C 1567, which determines the potential alkali-silica reactivity of combinations of cementitious materials and aggregates by accelerated mortar-bar method.

Lab Analysis:

1. NDOR analyzed the percentage of oxides from NDOR data history from previous recent years and compared five different oxide ratio combinations shown in Table 1 with ASTM 1567 results.

Table1.

Oxide Ratio				
$\%CaO/\%SiO_2$	$\%CaO/\%Al_2O_3$	$\%CaO/\%Fe_2O_3$	$\%SiO_2/Al_2O_3$	$\%SiO_2/Fe_2O_3$

The $\%CaO/\%SiO_2$ ratio was the only consistent oxide ratio when compared with ASTM C 1567 results. This confirmed the belief of the relationship between calcium and silica that benefits the prevention of ASR.

2. NDOR chose ten random 1PF blended cement samples to analyze the $\%CaO/\%SiO_2$ ratio. Three of the ten samples analyzed had significantly higher $\%CaO/\%SiO_2$ ratios than the other samples. It was expected that these samples with high $\%CaO/\%SiO_2$ ratios would fail ASTM C 1567 testing, because the NDOR database history of ASTM C 1567 showed that high $\%CaO/\%SiO_2$ ratio values correlated with high ASTM C 1567 results. The ASTM C 1567 test results verified failure.

3. NDOR blended in-house 12 samples with varying amounts of Class F Fly Ash within the percentage range according to NDOR specifications. The samples were composed of Type II cement from all three suppliers. The XRF results for these samples were used to determine an exact $\%CaO/\%SiO_2$ ratio value to use as a quality assurance.

Summary of Phase 2:

NDOR established the $\%CaO/\%SiO_2$ ratio as a quality assurance for blended cements.

Implementation:

NDOR follows the Quality Assurance in the Materials & Sampling Guide based on the Acceptance Policy for Portland and Blended Cements at the project level. The policy is based on the oxide ratio verification established by the correlation made by NDOR analysis. If the sample in question has a $\%CaO/\%SiO_2$ ratio above the predetermined limit, ASTM C 1567 will be run to confirm the blended cement meets NDOR specifications.

Every two years the XRF instrument is recalibrated for blended cements similar to ASTM C 114 "Standard Test Methods for Chemical Analysis for Hydraulic Cement" aiming to meet Table 1 requirements as close as possible. Previous Blended CCRL samples are used as the standards. The values used when calibrating are from the Final Report of the CCRL samples. These values in the report are determined by averaging the results submitted from all participants of the CCRL program. NDOR will re-establish the quality assurance ratio for blended cements after every re-calibration of the XRF instrument.