



THE EVALUATION OF THE ADDITION OF PHOSPHATIC CLAY IN CEMENT PASTE AND CONCRETE

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Abstract

Phosphatic clay is a by-product of the phosphate strip mining industry, and disposal is particularly a problem in Florida, USA. This waste material occupies about 100,000 acres of land which could be utilized for other causes. Thus, its potential utilization as a supplementary cementing material added to the cement paste matrix of concrete to produce higher strength would be beneficial for both the mining and construction industries. The waste clay contains calcium montmorillonite, which should react pozzolanically with the calcium hydroxide produced from the hydration reactions to produce additional C-S-H, the building block of concrete systems, and thus enhancing the mechanical properties of cement paste and concrete. The effects of phosphatic clay addition on the bulk properties of cement paste and concrete are investigated, and it is shown that moderate additions (5% replacement of cement by mass) can indeed

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produce a significant increase in strength. The effect of the modified paste on the interfacial transition zone in concrete is also observed.

1. Introduction

Phosphatic clay is a by-product of the phosphate mining industry when using a strip mining approach. In the US state of Florida, storage of this waste material occupies approximately 100,000 acres of land which could otherwise be utilized for other purposes [2]. Thus, its potential utilization as a supplementary cementing material added to cement paste and concrete would be a significant benefit for both the concrete and phosphate mining industries.

Since calcium silicate hydrate (C-S-H) is the primary component responsible for the strength of concrete, and produces a much stronger microstructure than calcium hydroxide (CH), it follows that increasing the proportion of C-S-H will result in a stronger material [1]. The addition of a pozzolanic material, such as waste phosphatic clay, can induce a reaction with the weaker calcium hydroxide which converts it into C-S-H, thereby increasing the density and strength of the concrete microstructure.

The reaction of cement with water is primarily responsible for the production of C-S-H, CH and other hydration products, while excess water beyond that which is needed for full hydration of the cement can lead to high porosity concrete with poor mechanical properties and impaired durability characteristics. The proportion of water in a concrete mixture is thus of utmost importance in the determination of both its early age and time dependent properties. The utilization of waste phosphatic clay comes with a complication, however. To be economically feasible, the waste material needs to be implemented as it is, with little modification. Due to the mining techniques used to extract the phosphate, this means that a significant amount of water will be included with the phosphatic clay and must be accounted for by modifying the amount of mixing water added separately. It is necessary in the determination of the water available for hydration of the cementitious materials and must be quantified prior to the implementation of phosphatic clay waste in cement paste and concrete to enhance properties.

2. Model

The waste phosphatic clay used in this experimentation was obtained from PCS Phosphate in White Springs, Florida. The biggest drawback faced in the

implementation of phosphatic clay waste as an additive to concrete is that the waste material contains a large amount of water, which could be detrimental to the concrete mixture if it is available during the mixing procedure. Hence the amount of water present in the waste clay must be determined for the preparation of cement paste and concrete samples.

It is also essential to determine the effect of clay impurities, as certain impurities might be dissolved in the water and could induce a detrimental effect on the resulting cement paste and concrete samples. This can be accomplished by performing an elemental analysis on the waste clay and comparing the results from various sources to determine any changes in composition. This experiment will help in determining whether any deleterious impurities are present in the water and shall assist in the determination of the amount of water present with the clay, thus serving as a guideline for the utilization of waste phosphatic clay in cement paste and concrete as a pozzolanic material.

3. Experimental Approach

Cement paste specimens were prepared at different proportions using Type I Portland cement from the Rinker Materials Miami plant, waste phosphatic clay from PCS Phosphate, and ordinary tap water. Concrete specimens were prepared using the same Type I Portland cement, a coarse limestone aggregate, fine aggregate and tap water in various proportions for determination of optimal ingredients and trends. For all specimen preparation, the waste phosphatic clay was obtained from PCS Phosphate Industries, but this waste clay was also compared (using X-ray fluorescence) to clay from Cargill Industries to illustrate differences in elemental composition. Specimens with various ingredients were also prepared for compression testing.

At the strip mining site, the waste clay is discharged at a very high water content (approximately 3% solids) which would make it virtually impossible to use in concrete. However, it was discovered that simple dredging of the effluent pond could reproducibly obtain waste clay at 15% solids. This latter value was chosen as the standard art which all of the specimen preparation would be conducted.

3.1. Procedure for preparing cement paste specimens

- (1) A quantity of diluted phosphatic clay was sampled and dried overnight in an oven at 110°C in order to remove all water from the specimen. This helped determine the exact proportion of solids present.

- (2) Using the results from Step 1 as a benchmark, a second sample of phosphatic clay was obtained from the same source and dried until it reached a 15% solids proportion. It was important to ensure that the exact proportion of solids was determined from any specific source before using diluted clay from that source. Otherwise, drying to 15% solids would be virtually impossible.
- (3) The correct quantities of cement and water were weighed out as per the mix design requirements for a 0.60 water to cementitious materials ratio. A basic sample batch size was designed around a cement content of 500 grams.
- (4) The exact amount of phosphatic clay waste required was then determined based upon the desired cement replacement rate (i.e., a 5% substitution required 25 grams of phosphatic clay and the amount of cement was reduced to 475 grams.
- (5) Once the required quantity of phosphatic clay was established, the necessary equivalent amount of waste material at 15% clay solids was determined. For example, if 25 grams of phosphatic clay was required, then 167 grams of waste materials at 15% solids was be needed.
- (6) The amount of water required by the mixture design was reduced by the amount of water obtained included with the waste material at 15% solids (i.e. $167 - 25 = 142$ grams of water in the added waste material). Therefore, the mixing water required was 158 grams ($300 - 142$).
- (7) The cement paste was then mixed using a Hobart table-top mixer (Model N50). The cement was placed in the mixer first. Then the mixing water and the 15% solids clay mixture were added at virtually almost the same time and the mixer was started.
- (8) The mixer was allowed to run for 4-5 minutes until homogeneity was achieved. If the mixture became too thick for the mixer to operate, then a superplasticizer was added (ADVA 100 by Grace Construction Chemicals).
- (9) The mixture was then removed and cast into either 2"x4" or 3"x6" cylinder molds, using a vibratory table to help remove voids and consolidate the paste.

- (10) After 24 hours, the specimens were removed from the cylinder molds and immersed in a lime saturated water solution for curing.
- (11) Mechanical testing was later performed at the specified testing dates according to the required curing times.

3.2. Procedure for preparing concrete specimens

- (1) The water to cementitious materials ratio required was determined and a mixture design was formulated in accordance with the design approach described in the PCA handbook on Design and Control of Concrete Mixtures [3]. The maximum aggregate size of the aggregate used was $\frac{3}{4}$ ".
- (2) Aggregate gradation was verified to be in accordance with ASTM standards.
- (3) The required amounts of phosphatic clay and waste materials, and the adjustment to the mixing water, were determined as per Steps (1)-(6) in Subsection 3.1.
- (4) The coarse aggregate was added to the mixer first, followed by the waste material and the remaining mixing water. The mixer was started and allowed to run for 2-3 minutes.
- (5) The cement was then slowly added to this mixture, followed by the fine aggregate. Mixing was continued for 4-5 minutes until homogeneity was achieved.
- (6) If the mix became too viscous to continue, then measured amounts of superplasticizer were added. The superplasticizer used in this study was again ADVA 100 from Grace Construction Chemicals.
- (7) Following the completion of mixing, the mixture was removed and cast into the 4"x8" cylinder molds, using a vibratory table to help remove voids and consolidate the concrete.
- (8) After 24 hours, the specimens were removed from the cylinder molds and immersed in a lime saturated water solution for curing.
- (9) Specimens were tested at their designated testing dates according to the required curing times.

3.3. Preparation of clay specimens for X-ray fluorescence

Elemental analysis was performed using a Phillips Model PW 2400 X-ray

fluorescence spectrometer, located at the Florida Department of Transportation State Materials Office. To study the presence and proportion of clay impurities, phosphatic clay from various sources was evaluated utilizing X-ray fluorescence to investigate the variation between sources. Phosphatic clay was obtained from PCS Phosphate Inc. at White Springs, Florida and Cargill Inc. at Bartow, Florida.

3.4. Compression testing of specimens

Compression testing performed for this research was conducted on an MTS 810 Material Testing System. The cement paste specimens were either 2"x4" or 3"x6" cylinders. They were tested at a displacement rate of 1.0000 mm/min, with a specified failure limit of 10 mm of displacement. The concrete specimens were 4"x8" cylinders and testing was performed at a displacement rate of 0.025 inches/minute. The absolute end level was specified as -1.000 inches. Both cement paste and concrete specimens were tested in displacement control. Prior to testing, both ends of the specimens were ground for uniformity. All tests were performed at room temperature (approximately 20-30°C). Figure 1 depicts the testing equipment and Figure 2 depicts the setup of a specimen before testing, with strain gauges mounted on the cylinder.

3.5. SEM analysis of specimens

The concrete specimens prepared with phosphatic clay were cut into small square specimens using a wafering saw and then polished to create a smooth finished surface to be analyzed by the SEM. The Hitachi EDAX environmental scanning electron microscope is utilized for analysis.

4. Results and Discussion

4.1. X-ray fluorescence

In this technique, an X-ray photon strikes the specimen surface, energizing and causing the ejection of a photoelectron, which is analyzed for its kinetic energy. The kinetic energy can then be used to identify the type of element present [4, 5].

From the results of the elemental analysis, it was observed from the virgin waste clay analysis that there were some minute differences between sources, though the clay elemental compositions remained essentially the same, suggesting that the source of the waste clay may not make a drastic difference in its pozzolanic activity. Table 1 contains the results for the waste clay from PCS Phosphate and Table 2 for the waste clay from Cargill.

4.2. Compression testing

Once the extent of water present with the waste clay was estimated and its implementation was understood, cement paste and concrete specimens were prepared with the addition of waste phosphatic clay for the determination of optimal amounts.

To study the effects of the addition of phosphatic clay in cement paste and concrete, 2"x4" cement paste specimens were prepared with the addition of phosphatic clay by replacing a portion of the Portland cement used as per the procedure discussed earlier. Specimens were tested in compression after 28 days of curing. It was observed that when 5% phosphatic clay was added, the strength of the specimen increased from those cast from standard cement paste. However, this trend did not continue at the 10% phosphatic clay replacement level, as the strength actually dropped compared to the specimens with 5% phosphatic clay. Beyond the optimal point, there is a shortage of calcium hydroxide present at that point in the cement matrix for the pozzolanic reaction and the clay could clump together or remain unreacted and serve as weak zones. Figure 3 depicts the compression testing results with the adjusted water to cementitious materials ratios for the specimens involved.

After observing the test results and trends for the cement paste specimens, it was decided to prepare concrete specimens with the additions of 5% and 10% waste clay as per the previously described procedure. The specimens were tested after 14, 28 and 56 days of curing and their trends were studied in detail. The required amounts of specimens were prepared keeping in mind that at least three specimens were required at each age of curing for every combination of materials. The stress-strain plot for each combination was then determined as an average of three test results.

Time is a variable that must be considered when dealing with pozzolanic modification of concrete mixtures. The pozzolanic reaction, by nature, is a delayed reaction. The CH must form first before the pozzolanic reaction can even commence as the reaction of C_3S and C_2S leads to the formation of CH as seen in cement chemistry. Thus, the full effect of the clay addition will take somewhat longer to manifest and hence 14, 28 and 56 days were considered the appropriate time frames. Figures 4, 5 and 6 depict the results of the additions of 5% and 10% waste clay, organized such that each graph shows all of the different combinations at the same age (14, 28 and 56 days).

Figure 4 depicts the results for specimens at 14 days. The concrete containing the 5% waste clay mixture combination easily performed better than the control mix, exhibiting significantly higher strength and slightly increased ductility. The specimen containing 10% waste clay exhibited much lower strengths but showed gains in post peak ductility. Similar trends are observed at 28 days, shown in Figure 5.

Similar trends are again noticed at 56 days. The 5% phosphatic clay waste specimen is now showing a much larger gain in strength with the production of more calcium hydroxide (CH) from the cement hydration reactions and the conversion of more CH to C-S-H with the pozzolanic reaction. The drawback to this, however, is that the samples have started to behave in a more brittle fashion. Figure 6 depicts the results for specimens at 56 days.

It can be concluded from the results in Figures 4, 5, and 6 that the addition of waste phosphatic clay by itself is capable of increasing the strength of the concrete given sufficient time.

4.3 Effects of waste clay addition on the interfacial transition zone (ITZ)

The concrete specimens containing phosphatic waste clay were analyzed for modifications to the concrete-aggregate interfacial transition zone (ITZ).

Concrete specimens with 2% waste phosphatic clay were examined to study the effect of the addition of waste phosphatic clay on the ITZ. Modifications to the ITZ in concrete could be an indicator as to the enhancement in strength of the concrete with time. For the concrete with 2% waste clay, it was observed that packing near the aggregate was dense and the ITZ was hard to identify. This could lead to lower permeability (and thus increased durability) and improved compressive strength. Figure 7 depicts the ITZ at 2500x magnification.

5. Conclusions

It can be summarized from this paper that the addition of waste phosphatic clay is a feasible option for addition into cement paste and concrete. Waste clay addition into concrete can also positively affect its mechanical properties. The following conclusions can be drawn from the testing results discussed:

- From the elemental analysis, it can be inferred that the minute quantities of waste material present in the clay should not affect the pozzolanic activity of the waste clay in cement paste and concrete.

- The compression testing results for the various specimens indicate that the waste clay is reacting pozzolanically and, as a result, assisting in the improvement of the compressive strength of concrete.
- From the SEM pictures of the interfacial transition zone for concrete containing waste clay, it can be concluded that the modified paste produces a denser contact area with the aggregate and thus reduces porosity in the interfacial transition zone.
- The addition of phosphatic clay into concrete could be a feasible option for disposing of a waste material while simultaneously providing a benefit to the concrete industry.

The results thus lead toward the formation of guidelines for the utilization of phosphatic clay in cement paste and concrete in a more effective manner.

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Figure 1. Compression testing machine-MTS Material Testing System Model 810.



Figure 2. Setup prior to compression testing showing the strain gauges on the specimen.

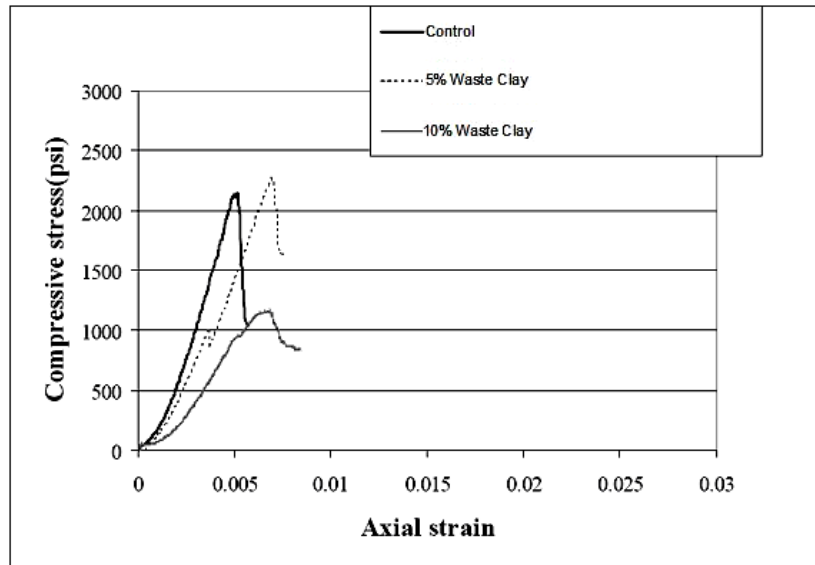


Figure 3. Effect of phosphatic clay addition on the stress-strain behavior of cement paste.

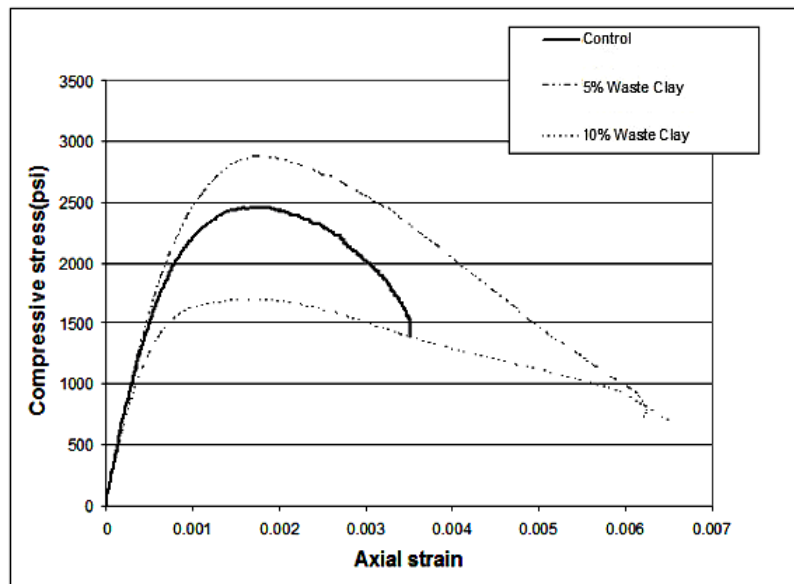


Figure 4. Effect of phosphatic clay addition on the stress-strain behavior of concrete after 14 days of curing.

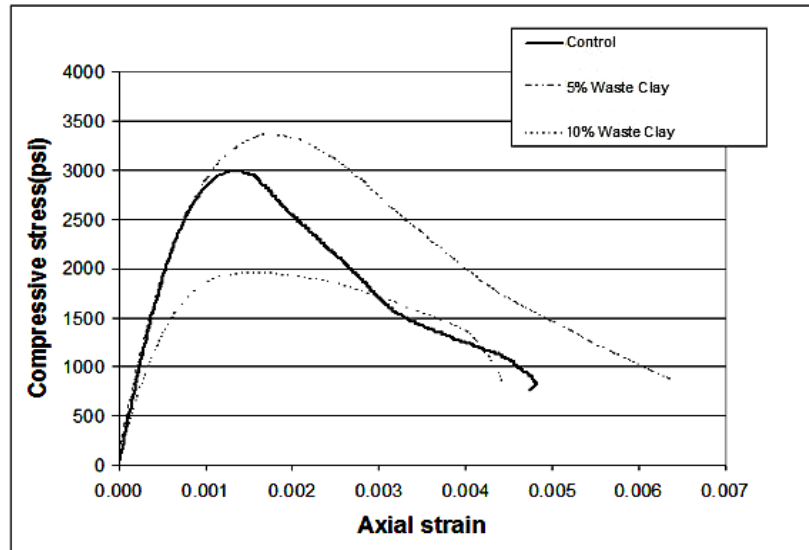


Figure 5. Effect of phosphatic clay addition on the stress-strain behavior of concrete after 28 days of curing.

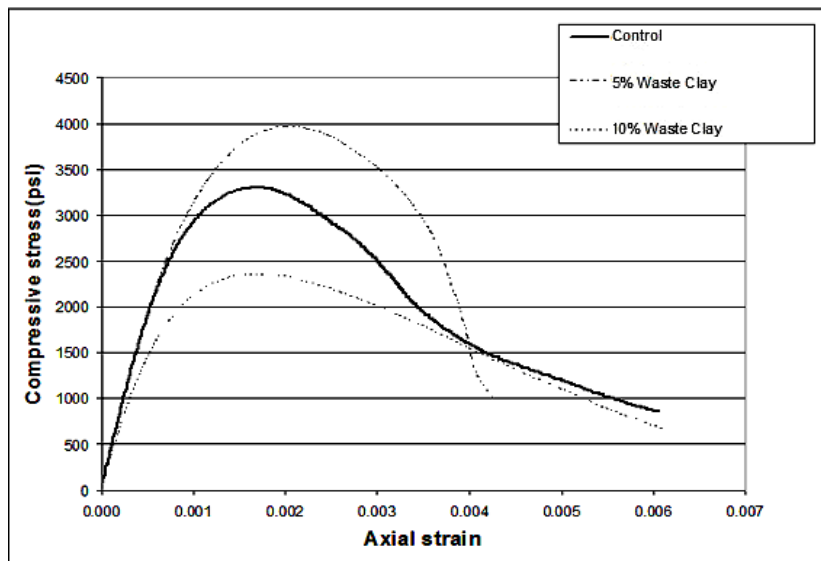


Figure 6. Effect of phosphatic clay addition on the stress-strain behavior of concrete after 56 days of curing.

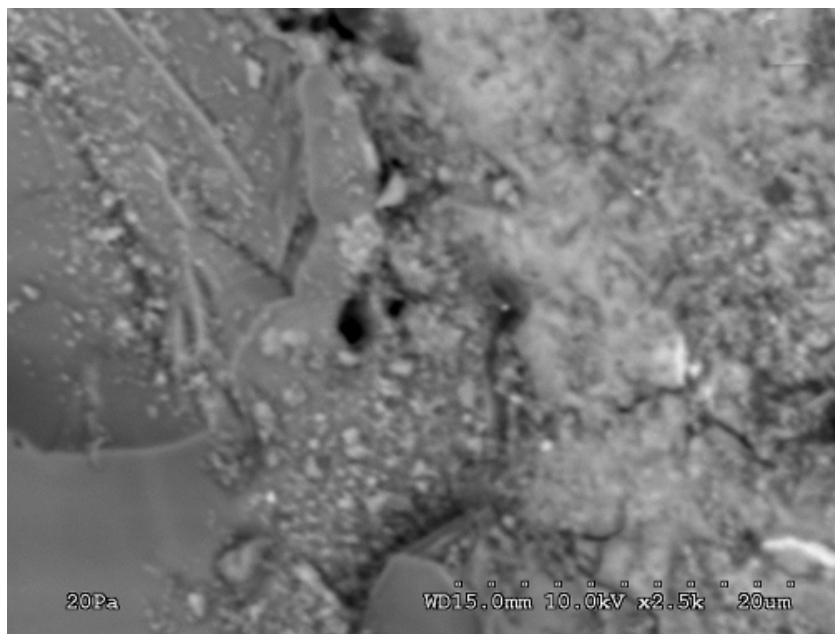


Figure 7. Concrete containing 2% phosphatic clay at 2500x magnification.

Table 1. X-ray fluorescence results for waste clay from PCS phosphate

Analyte	Compound formula	Concentration
Al	Al	5.24
Si	Si	22.64
P	P	12.22
S	S	0.30
K	K	2.21
Ca	Ca	36.18
Ti	Ti	1.40
Fe	Fe	19.50
Sr	Sr	0.30
	Total	100.00

Table 2. X-ray fluorescence results for waste clay from Cargill

Analyte	Compound formula	Concentration
Al	Al	5.39
Si	Si	19.54
P	P	11.81
S	S	0.64
K	K	2.06
Ca	Ca	30.03
Ti	Ti	1.14
Fe	Fe	27.18
Sr	Sr	0.27
Zr	Zr	0.03
Sn	Sn	0.52
Ba	Ba	0.23
Na	Na	1.16
	Total	100.00