

Determination of Expansion Potential of Coal Combustion By-Products

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ABSTRACT

Expansion of some coal combustion by-products (CCBs) is of great concern, especially when these materials are utilized as engineered fills or other bulk placements. Some CCBs, especially some fly ashes, have the potential to swell, and the expansion or swelling can result in failure of the fill to meet performance criteria. The potential for a CCB to swell or expand can be determined using a simple test for bulk density. Initially, the density of as-managed fly ash is determined. The fly ash is then placed on a rotation or agitation device and hydrated using distilled, deionized water for a desired length of time. Generally, the fly ash is hydrated for 30 days, after which it is filtered, dried in an oven below 48°C, and the final hydrated density determined. A negative change in the density from the as-managed or as-received sample to the hydrated sample can be interpreted as swell or expansion potential of the fly ash. Subsequently, the 30-day hydrated ash can be rehydrated for 30 additional days and the density re-determined, which will provide insight into the long-term expansion potential of the fly ash. Helium–air pycnometry, a quick and non-destructive method, was used for density determinations, although other methods are available. Quantitative X-ray diffraction was used to determine specific species responsible for the expansion observed.

INTRODUCTION

Following an evaluation of American Society for Testing and Materials (ASTM) methods to determine swell and expansion of materials, the Energy & Environmental Research Center (EERC) concluded that common test methods relied on similar material properties to evaluate expansion. The tests were generally designed for evaluating soils, such as expansive clays, but even with modifications for use with varying materials, relied on one-dimensional expansion of compacted samples. No existing standard expansion test appropriate for the properties of coal combustion by-products (CCBs) was identified. Several expansion mechanisms have been proposed for reactive CCBs. Reactive CCBs include moderate- to high-calcium fly ash, fly ash–dry flue gas desulfurization mixtures, and fluidized-bed fly ash. The proposed expansion mechanisms in these materials differ greatly from expansion mechanisms associated with soils, so the application of expansion tests designed for soils has the potential to provide inaccurate information.

The EERC has hypothesized that ettringite formation is a key mechanism for expansion in reactive CCBs. Ettringite is a mineral with the nominal composition $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$. Ettringite crystal formation is initiated by a source of soluble calcium, aluminum, and sulfate; a pH over 11.5; and plenty of water. The EERC has hypothesized that ettringite crystals can form and grow into even extremely small voids in well-compacted material and may not press directly on neighboring particles. As a result, dimensional changes may not occur in laboratory test specimens even though expansive reactions have occurred.

The EERC has developed a test to predict expansion potential for CCBs. The hypothesis for the test development is that if mineralogical and compositional changes in a material such as fly ash result in expansion, the mass must also experience a respective negative change in bulk density. The determination of bulk density of a mass of ash before and after hydration affords a rather simple and reliable means of determining potential for expansion. This paper discusses the method development. The EERC continues to evaluate the method presented here.

METHODS

The proposed method involves simple laboratory procedures: density measurements, hydration of the test sample, and drying of the sample in a controlled environment. The proposed method requires the following steps:

- 1) Determine the density of the test sample.
- 2) Hydrate the sample using a specific liquid-to-solid ratio for a prescribed time period with intermittent mixing.
- 3) Collect the hydrated sample by filtering.
- 4) Dry the hydrated sample at $<48^\circ\text{C}$ to remove free water but not destroy the ettringite structure.
- 5) Determine the density of the hydrated sample.

The density values are then compared. A reduction in sample density with hydration indicates potential for expansion. No change or an increase in sample density with hydration indicates that the sample does not have potential to expand.

Two methods were employed to determine density: the ASTM C188-95, Standard Test Method for Density of Hydraulic Cement and helium–air pycnometry.

ASTM C188-95, Standard Test Method for Density of Hydraulic Cement

This test utilizes LeChatelier's principle of displacement of a liquid to determine bulk density of a finely powdered material. In this test, kerosene is the liquid used, and

commercially available LeChatelier bottles are used. Densities were determined on samples dry and following hydration.

Helium–Air Pycnometry

Helium–air pycnometry is a quick and reliable tool for determining bulk densities of solid materials. A helium–air pycnometer is a gas displacement pycnometer, which is an instrument that measures the volume of solid objects of irregular or regular shape whether powdered or in one piece. Therefore, helium–air pycnometry is a well-suited technique for CCBs. The pycnometer determines skeletal volumes by observing the reduction of gas capacity in the sample chamber caused by the presence of the given sample. Helium, as well as other suitable gases, penetrates the smallest pores and surface irregularities common in CCB samples, allowing the volume obtained to be used for the computation of the ultimate theoretical density of the solid comprising the sample. The method is nondestructive so the sample can be reused. The EERC utilized a Model 1305 Micromeritics Multivolume Pycnometer for density determination.

As-received CCBs were tested for density using ASTM C188-95, and then the same materials were hydrated, dried at <48°C, and retested. Reduction in density can be related to swell potential based on proposed expansion mechanisms. Since the initiation of the use of density as a means of determining swell potential, the ASTM C188-95 test for density has been replaced by helium–air pycnometry. This test is highly reproducible, nondestructive, and requires a smaller sample size than the ASTM C188-95 method.

EXPERIMENTAL

A sample set was assembled for use in method development. The sample set included a variety of CCBs to represent low, moderate, and highly reactive materials that the method would ultimately be used to evaluate. The sample descriptions are included in Table 1.

As already noted, the proposed method involves the following steps using simple laboratory procedures:

- 1) Determine the density of the test sample.
- 2) Hydrate the sample using a specific liquid-to-solid ratio for a prescribed time period with intermittent mixing.
- 3) Collect the hydrated sample by filtering.
- 4) Dry the hydrated sample at <48 °C to remove free water but not destroy the ettringite structure.
- 5) Determine the density of the hydrated sample.

Density testing was performed using standard laboratory methods appropriate for CCBs, but the hydration procedure and duration and the appropriate drying needed to be determined.

Ten different CCB samples from a coal-fired power plant were evaluated for expansion potential. The samples consisted of varying depth composites of ash from a pond and ponded ash that had been stacked for dewatering. Densities of the material before and after hydration were initially to be determined using ASTM C188-95. Shortly after the project began, a Model 1305 Micrometrics Multivolume Pycnometer became available for use. The values reported in this document are the values obtained from the helium–air pycnometer. For this work, helium was the gas used in the density determination. The helium–air pycnometer was chosen for this research for several reasons. Using kerosene in LeChatelier bottles provides one data point for each sample. Additionally, after saturation with kerosene, the sample cannot be reused. Helium–air pycnometry is a nondestructive technique and a single sample can be tested numerous times. For this project, six individual measurements were made on each sample. Another advantage of this technique is that sample densities can be determined, the sample can be dried for an additional period of time, and the test can be repeated. This assures the highest degree of accuracy and provides reliable data.

Hydration was carried out by placing 150 g of dry ash into a bottle with approximately 200 mL of distilled, deionized water. The contents were mixed using end-over-end rotation at 30 rpm. Rotation was continuous for a week and then intermittent for the remainder of the hydration time. For intermittent rotation, a microprocessor-based on-off timer that turned the rotator on for 1.5 hours every 4 hours. We assumed that the likelihood for the material to form a monolith had passed after 1 week of rotation and that intermittent rotation was adequate to prevent the solids from caking to the bottom of the bottles. At the end of the 30-day hydration period, the ash was filtered through coarse filter paper in a Büchner funnel and was washed with distilled, deionized water. Air was then drawn through the ash to remove excess water. The wet ash was placed into an evaporating dish and placed in an oven at $<48^{\circ}\text{C}$. Drying at $<48^{\circ}\text{C}$ allows for the free water to be driven off of the hydrated ash without affecting the crystalline structure of any ettringite that may have formed. Heating was continued until the sample reached a constant weight. At that time, the bulk density of the hydrated ash was determined using helium–air pycnometry.

RESULTS AND DISCUSSION

Data for this project are shown in Table 1. Negative numbers for % change indicate swell potential.

The ponded ash challenged the experimental method because of the inconsistent particle size and moisture content. Overcoming the challenges associated with these materials facilitated the ongoing development of the EERC proposed method. The use

Table 1. Helium Pycnometer Calculations Indicating Swell Potential for Composite Poned Ash Samples

Sample	Depth (feet)	Unhydrated	Hydrated	Abs. Change	% Change
03-090	3.5–5.5	2.4384	2.4841	0.0457	1.87%
03-091	8.5–10.5	2.4629	2.4790	0.0161	0.65%
03-092	13.5–15.5	2.4996	2.5285	0.0289	1.16%
03-093	18.5–20.5	2.4908	2.4466	-0.0442	-1.77%
03-094	23.5–25.5	2.4956	2.4953	-0.0003	-0.01%
03-095	28.5–30.5	2.4628	2.4932	0.0304	1.23%
03-096	33.5–35.5	2.4285	2.4372	0.0087	0.36%
03-097	38.5–40.5	2.5165	2.5161	-0.0004	-0.02%
03-045	43.5–45.5	2.4592	2.4732	0.0140	0.57%
03-024	Stacked ash	2.5492	2.5881	0.0389	1.53%
Average % Change (poned ash)		0.34 %			

of helium–air pycnometry greatly increased the accuracy and precision of the measurements. Each number in Table 1 is actually an average of about 12 different measurements. The researchers associated with this effort have drawn the preliminary conclusion that the average calculated 0.34% overall expansion potential is not significant. The material tested is expected to be well-suited for use in structural fill applications.

CONCLUSIONS

The swell potential in CCBs can be easily predicted using this simple method. Although it determines potential for swell, this is an important consideration when deciding if a material is suitable for use in structural or other engineering applications. Conventional swell tests as applied to soils can be misleading when used with CCBs. This may be due to ettringite crystals, which are responsible for swell, growing into void spaces, thus negating changes in dimensions in laboratory specimens. The use of changes in density as an indicator of expansion potential avoids the use of physical dimensional changes in a sample specimen, which may provide misleading results when evaluating CCBs.

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REFERENCES

[1] ASTM C 188-95, Section 4, Volume 04.01, pp 181-182, Standard Test Method for Density of Hydraulic Cement, 2002.