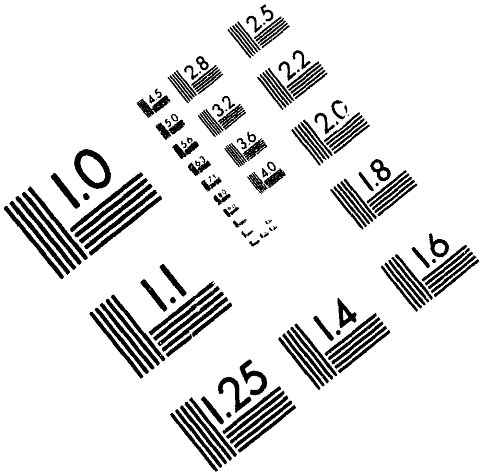
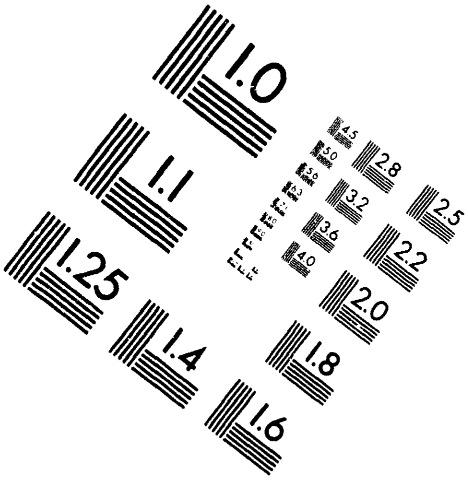


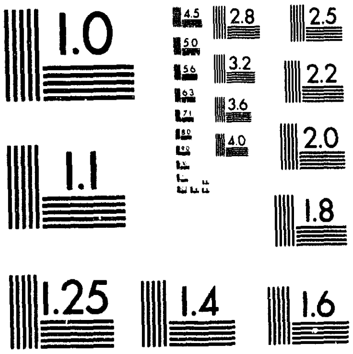


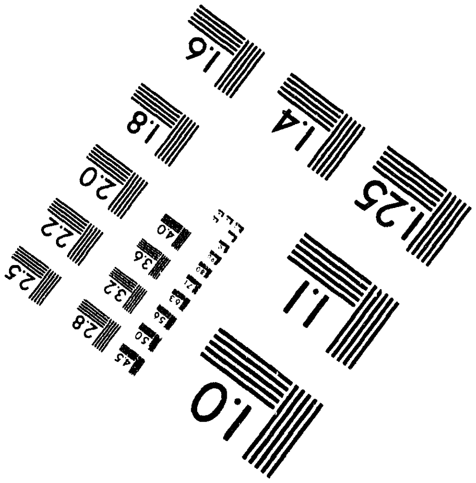
AIIM

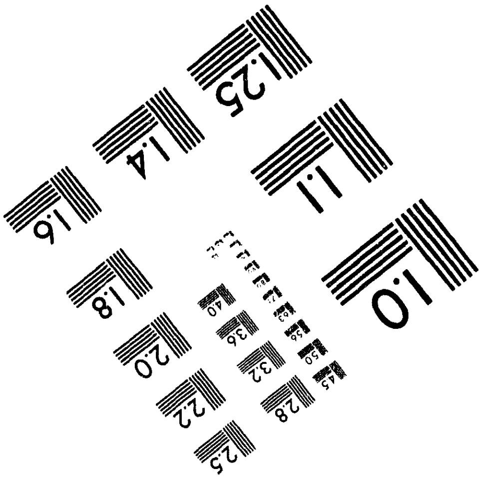
Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

301/587-8202







MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

Report for the period 4/1/94 to 6/30/94

DoE Grant DE-FG22-91PC91302

HYDROTHERMAL REACTIONS OF FLY ASH

Paul W. Brown
136 MRL
Penn State University
University Park PA 16802

ABSTRACT

The reactions which occur when fly ash is treated under hydrothermal conditions are being investigated. This is being done for two primary reasons. The first of these is to determine the nature of the phases that form, to assess the stabilities of these phases in the ambient environment and, finally, to assess whether these phases are capable of sequestering hazardous species. The second reason for undertaking this proposed study is that, depending on the composition of the ash and the presence of selected additives, it may be possible under hydrothermal conditions to form compounds which have cementitious properties.

Formation of four classes of compounds, which bracket likely fly ash compositional ranges, have been selected for study. These are calcium silicate hydrates, calcium silicosulfates, calcium aluminosulfates, and alkali aluminosilicates. The specific compounds fabricated will be determined and their stability regions assessed. As a part of stability assessment, the extent to which selected hazardous species are sequestered will be determined. Finally, the cementing properties of these compounds will be established.

US/DOE Patent Clearance is not required prior to the publication of this document.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ps

PROGRESS

During the last quarter, the hydrothermal behavior of tobermorite from fly ash were studied. Tobermorite ($Ca_5Si_6H_2O_{18}\cdot 4H_2O$) was successfully synthesized from fly ash-based materials by adjusting the bulk compositions to that of the systems made with the pure starting materials. Tobermorites have a layer structures and were discovered as a new group of cation exchangers, which exhibit partial exchange of structural Ca^{2+} for divalent metals, such as Co^{2+} and Ni^{2+} etc. [Al+Na]-substituted tobermorites have been shown to have reversible exchange and high selectivity for alkali cations such as Cs. Therefore, tobermorites synthesized from fly ash waste forms could be recognized as materials with potential applications in heavy metal removal from aqueous solutions. Accordingly, the kinetics of formation and morphology of tobermorite from class F and C fly ash have been studied.

The heat evolved during the hydrothermal reactions of class F fly ash containing different alkali concentrations were measured. The samples contained 46% Class F fly ash, 36% CaO, 18% SiO_2 as weight percentages. The results correspond with the data of XRD which suggests that alkali increase the kinetics of formation of tobermorite. The rates of heat evolution during the first hour after mixing are shown in Figure 1. Only single heat evolution peaks, which occur immediately after mixing, were observed. The reaction is accelerated with increasing alkali concentration. The total area under the mixing peak represents the total heat evolved during this initial period. It is observed that total heat remains about the same after first six hours of reaction. The morphology of tobermorite from in Figure 2 shows that it has a shape of flat plate.

Diffraction patterns of samples using Class C fly ash as the starting materials show that tobermorite forms after 12 hours in 0.80M NaOH solution, however, when this reaction takes place in 0.13M NaOH solution tobermorite cannot be detected up to 7 days. It is suggested that alkali plays a very important role in the formation of tobermorite. The rates of heat evolution during the first hour after mixing is shown in Figure 3. The samples contain 68% Class C fly ash, 17% CaO, 15% SiO_2 in weight percentages. The reaction is again accelerated by alkali, and the total heat also increases at first six hours of reaction. The morphology of tobermorite from SEM micrographs in Figure 4 shows that it has a needle-like morphology, and the particles of fly ash becomes fully surrounded by tobermorite after 24 hours of reaction. After 7 days of reaction, the morphology of tobermorite in figure 5 shows that it has a variety of forms ranging from fibers to flat plates.

QUANTIFIABLE OUTPUTS

A paper by W. Ma, D. Sample, R. Martin and P.W. Brown, entitled "Calorimetric Study of Cement Blends Containing Fly Ash, Silica Fume, and Slag at Elevated Temperature," has now accepted for publication in *Cement, Concrete, and Aggregates*.

PLANNED WORK

The emphasis of study is to establishing the stabilities of the phases formed by the hydrothermal reactions of fly ash and to establish their abilities to sequester heavy metals.

Specifically, the study of the uptake of selected RECRA heavy metals and of the high temperature phase stabilities of cementing compounds is continuing. A range of samples containing heavy metals are being prepared. These have variable Ca/Si ratios, and the ability of calcium silicate hydrate to sequester heavy metals depending on this ratio is being established. At the terminal Ca/Si ratios, calcium silicate hydrate coexists in equilibrium with excess SiO_2 or in equilibrium with excess $Ca(OH)_2$. As calcium silicate hydrate is exposed to natural waters, its composition shifts to lower Ca/Si ratios because Ca tends to be extracted due to the formation of $CaCO_3$. Thus, it is important to establish if this composition change in calcium silicate hydrate will also result in the release of heavy metals.

Heavy metals classified as cations (substituting for calcium) and oxyanions (substituting for silica) are being investigated; the cations include Ag^+, Sr^{2+}, Ba^{2+}, and Pb^{2+}, and the oxyanions include CrO_3^{3-}, AsO_4^{3-}, and SeO_3^{2-}. The goal of these experiments will be to determine equilibrium invariant points between the C-S-H and the heavy metals, as well as to show the kinetics of the reactions. Experiments are being conducted over a range of temperatures. Further work with the calcium aluminate hydrate with these other metals will also be conducted. Future work will focus on identifying the phases formed in these solutions, synthesis of pure phase batches of them, and combining them with the C3S or C3A for the final equilibrium studies. Solutions extracted from these solutions will then be analyzed to determine the equilibrium conditions.

We anticipate several additional, peer reviewed publications based on these ongoing studies.

Figure 1

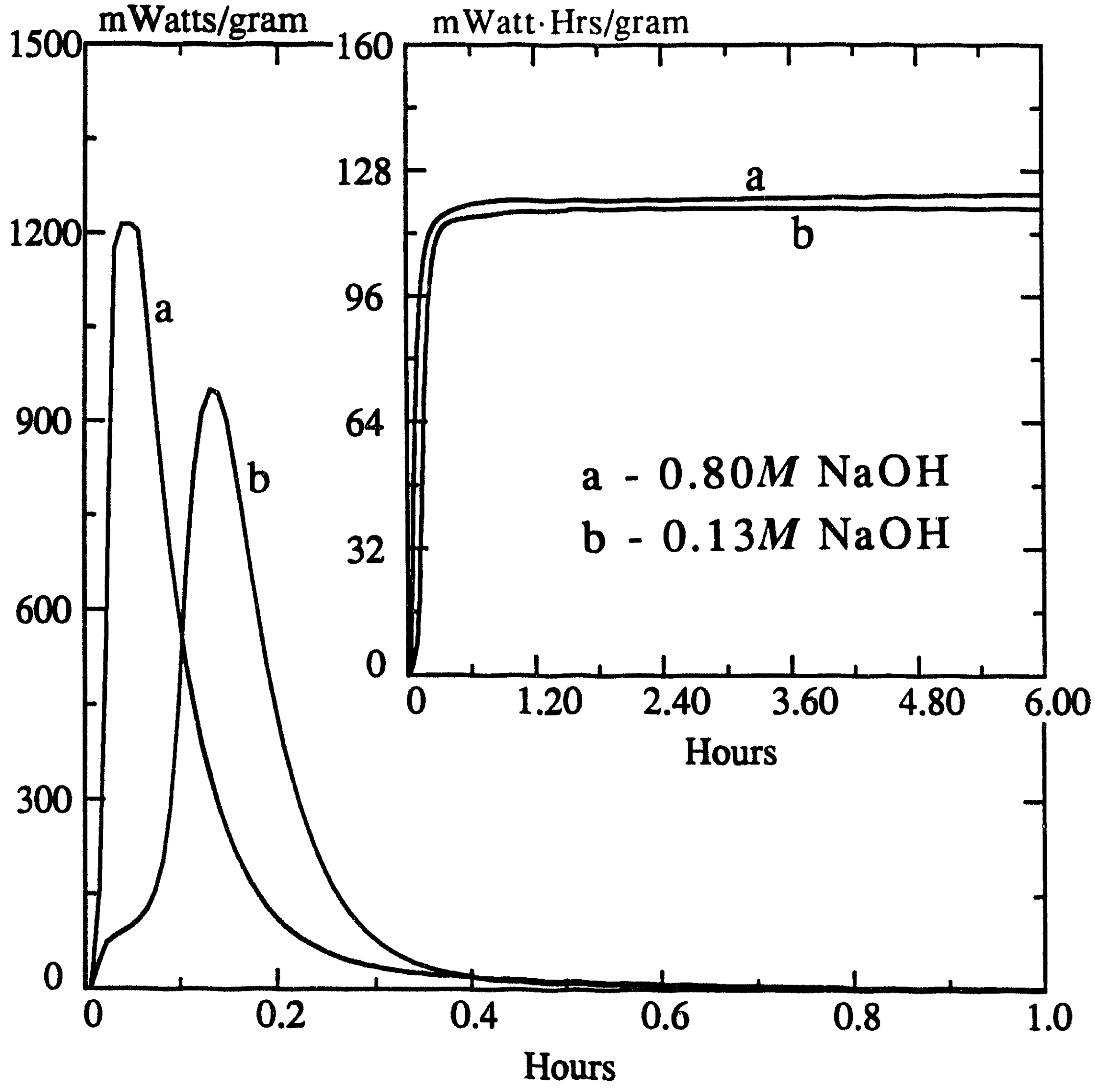

mWatts/gram
1500
1200
900
600
300
0
0
0.2
0.4
0.6
0.8
1.0
Hours
a
b
mWatt·Hrs/gram
160
128
96
64
32
0
0
1.20
2.40
3.60
4.80
6.00
Hours
a
b
a - 0.80M NaOH
b - 0.13M NaOH

Figure 2

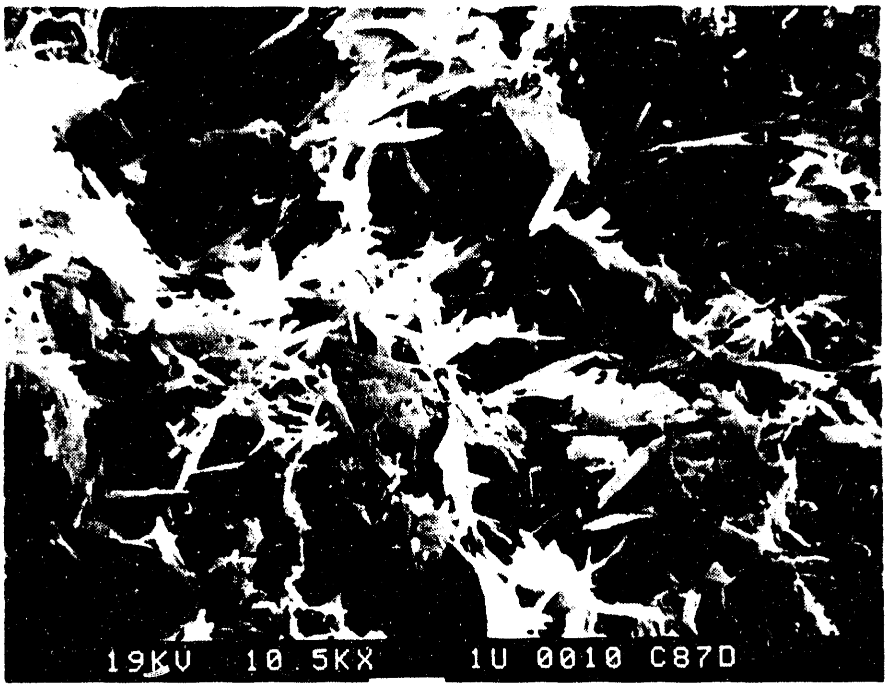


Figure 3

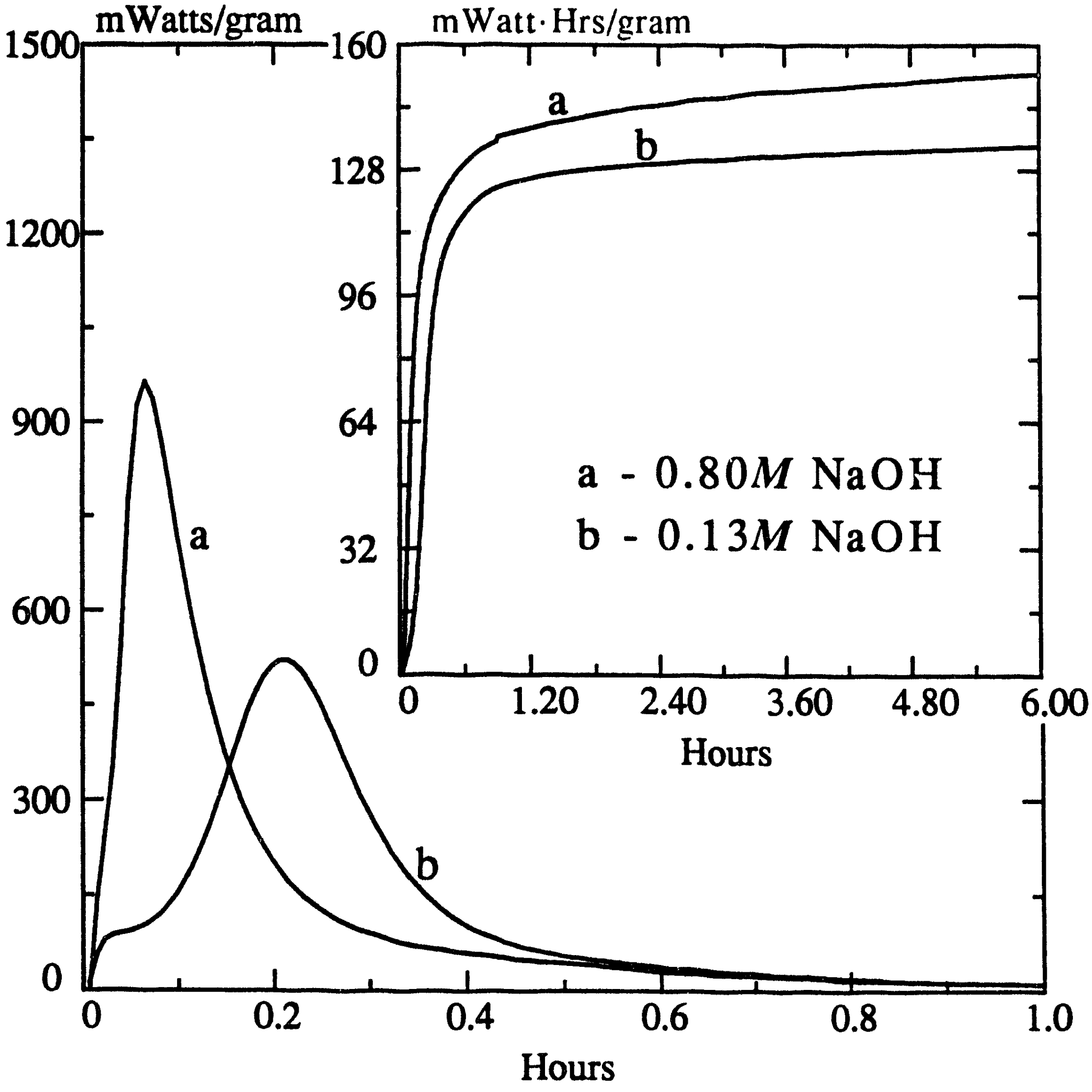
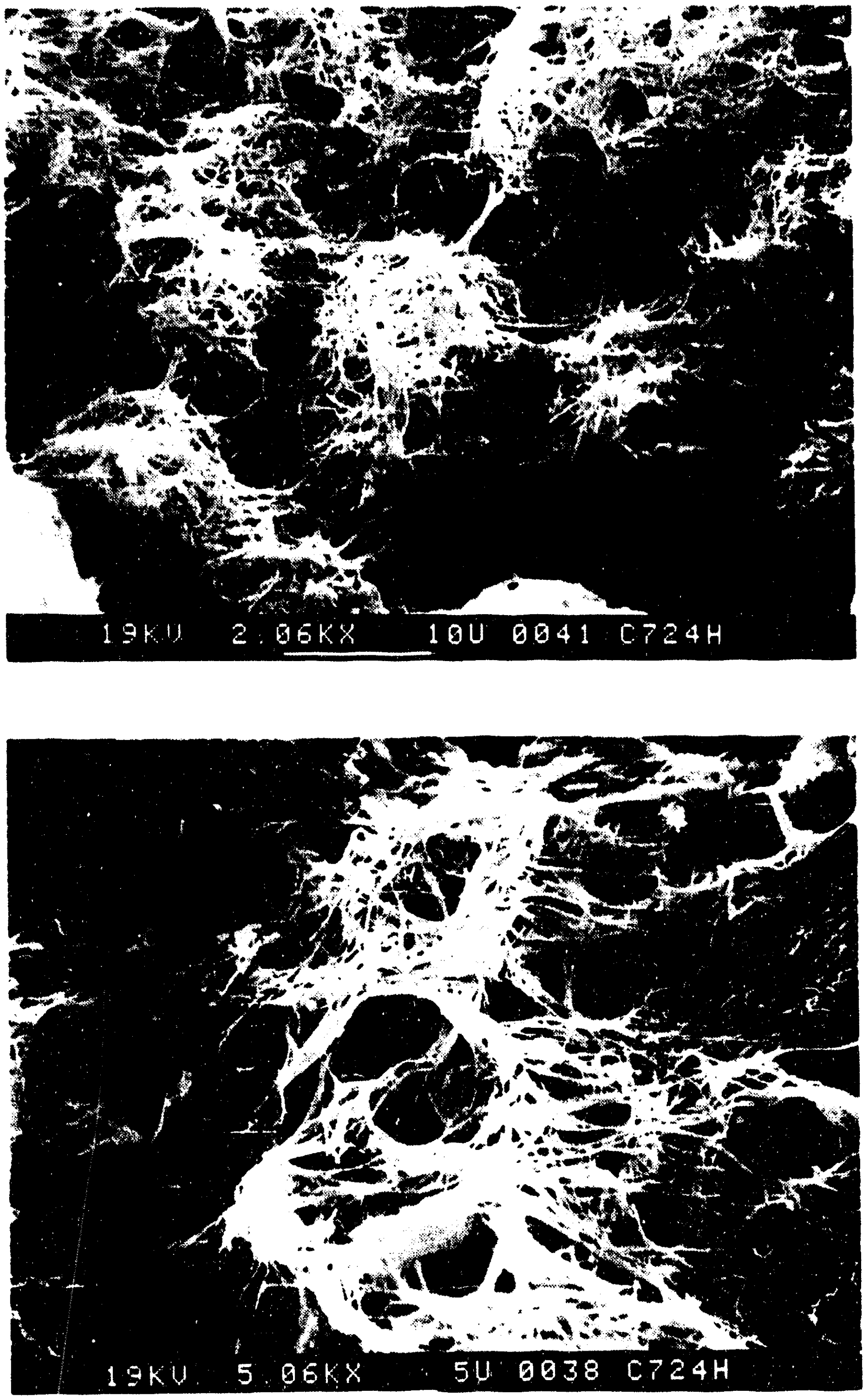

mWatts/gram
1500
1200
900
600
300
0
0
0.2
0.4
0.6
0.8
1.0
Hours
a
b
mWatt·Hrs/gram
160
128
96
64
32
0
0
1.20
2.40
3.60
4.80
6.00
Hours
a
b
a - 0.80M NaOH
b - 0.13M NaOH

Figure 4



24 hrs

Figure 5

7 days

Reporting Checklist

Marilyn Keane
PM-01, MS 922-206
U.S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

Norey B. Laug
Contract Specialist
AD-22, MS 921-118
U.S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

Office of Technology Transfer
Attn: Kay Downey
Mail Stop 58-M217
U.S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

DATE

FILMED

10/12/94

END