Combustion Byproducts Recycling Consortium

Combustion Byproducts Recycling Consortium

Quarterly Project Status Report
for the period
October 2005 through December 2005

Submitted to:

U.S. Department of Energy
National Energy Technology Laboratory
P.O. Box 10940
626 Cochrans Mill Road
Pittsburgh, PA 15236-0940

Submitted by:

Tamara Vandivort, Consortium Manager
National Mine Land Reclamation Center
West Virginia University
P.O. Box 6064
Morgantown, WV 26506-6064

Report Issued
January 2006

DOE Award Number: DE-FC26-98FT40028

Principal Investigator:
Paul Ziemkiewicz, Director
National Mine Land Reclamation Center
West Virginia University
Morgantown, WV 26506-6064

Combustion Byproducts Recycling Consortium
a program of West Virginia University
in cooperation with the U.S. Department of Energy
National Energy Technology Laboratory

January 18, 2006

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National Energy Technology Laboratory
U.S. Department of Energy
P.O. Box 10940
Pittsburgh, PA 15236-0940

RE: Cooperative Agreement DE-FC26-98FT10028

To Whom It May Concern:

Enclosed please find 3 copies of the quarterly project status report for the reporting period of October 2005 through December 2005. I hope this report meets with your approval.

If you have any questions, please do not hesitate to contact me. I can be reached at (304) 293-2867 x5448 or through email at tvandivo@wvu.edu.

Sincerely,

Tamara Vandivort
Program Coordinator

Enclosures

Cc: Bill Aljoe, DOE-NETL Program Manager

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Replaces EIA-459F
All Other Editions Are Obsolete

OMB Control
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U.S. DEPARTMENT OF ENERGY

FEDERAL ASSISTANCE PROGRAM/PROJECT STATUS REPORT

1. Program/Project Identification No.	2. Program/Project Title	3. Reporting Period
DE-FC26-98FT40028	Combustion Byproducts Recycling Consortium	10-1-05 through 12-31-05

4. Name and Address
West Virginia University Research Corp.
886 Chestnut Ridge Road, Room 202, PO Box 6845
Morgantown WV 26506-6845

5. Program/Project Start Date
8-31-06

6. Completion Date

7. Approach Changes

[X] None

8. Performance Variances, Accomplishments, or Problems

Please see attached project status report

[X] None

9. Open Items

[X] None

10. Status Assessment and Forecast

[X] No Deviation from Plan is Expected

11. Description of Attachments

[ ] None

12. Signature of Recipient and Date
[signature] 1/25/06

13. Signature of U.S. Department of Energy (DOE) Reviewing Representative an

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CBRC National Center Quarterly Progress Report

Submitted by: Tamara Vandivort
Consortium Manager, CBRC

CBRC National Center Report
for
October - December, 2005

Submitted by
Tamara Vandivort
CBRC Consortium Manager

Request for Full Proposals (RFP)

The deadline for receiving full proposals was set for December 15, 2005. Nineteen applicants were invited to submit full proposals and all nineteen submitted. Full proposals were placed on a secure website. Reviewers (CBRC National Steering Committee members) who signed confidentiality agreements were given access to the web site to review the full proposals. Full proposals were available for review and instructions and evaluation criteria were provided to the reviewers on December 20, 2005.

National Steering Committee Scheduled to Meet

The CBRC National Steering Committee (NSC) is scheduled to meet February 2, 2005 in Austin, Texas. The primary purpose of the meeting is to select full proposals to recommend to DOE-NETL for funding. The agenda is listed below:

Combustion Byproducts Recycling Consortium
National Steering Committee Meeting
Thursday, February 2, 2006
8:00 AM - 3:00 PM
Senate Room
Omni Hotel
Austin, TX

Agenda

8:00 AM	Continental Breakfast Provided	
	Welcome and Opening Remarks	*Paul Ziemkiewicz, Director National Center*
	Explanation of the Day's Agenda Materials, Timeline, and Program Update	*Tamara Vandivort, Consortium Manager*

8:20 AM	DOE-NETL Perspective for the CBRC Program	*William Aljoe, DOE-NETL COR*
8:40 AM	Discussion of the Full Proposals Western Region Midwestern Region Eastern Region	*Paul Ehret, NSC Chair* *Debra Pflughoeft-Hassett; Paul Chugh; Jim Hower, Regional Directors*
9:45 AM	**Break**	
10:00 AM	Continuation of Discussion of the Full Proposals	
11:30 AM	Working Lunch Provided	
1:00 PM	Selection of the Projects to Recommend to DOE-NETL for funding	*Paul Ehret, NSC Chair*
2:00 PM	Ways to Measure Program Success	*Paul Ziemkiewicz, Director* *Paul Chugh, Jim Hower, Debra Pflughoeft-Hassett, Regional Directors*
2:45 PM	Other CBRC Business	*Tamara Vandivort, Consortium Manager*
3:00 PM	Adjourn	

The meeting will be held in conjunction with the American Coal Ash Association (ACAA) meeting at the Omni Hotel, Austin. The National Center worked with ACAA to schedule the facility and meeting materials are being developed.

Outreach Activities

Low-Cost, Reliable Energy and Chemical Feedstocks for Energy-Intensive Industry Clusters: Feasibility Study of a Coal-Fired Co-Generation Facility in Marshall County, WV

The economic analysis and comparison of the generation cases was finalized. A draft final report has been prepared and is currently under review.

Web Site

The web site was updated on an on-going basis as new information, events, and final reports were received.

Quarterly Newsletter, *Ashlines*

The Fall, 2005 issue of Ashlines was completed. (See Appendix A.)

Project Final Reports and Papers

Two final reports were received on the following projects and can be found in Appendices B and C, respectively:

02-CBRC-E10: *Commercialization of Production Foundry Molds Made from CCBs for High Volume Automotive Applications*; Robert M. Purgert, Energy Industries of Ohio, Principal Investigator.

00-CBRC-M04: *Crushed Aggregates from Class C Fly Ash*; Dr. Anil Misra, University of Missouri, Principal Investigator.

Plans for Next Quarter

Budget Modification

Following the February 2, 2006 meeting at which the steering committee makes its recommendations as to which proposals should be funded, a budget modification will be developed and sent to DOE-NETL for consideration. This modification will include both administrative budgets for national and regional centers and project awards. The work period covered by this modification will be for September 1, 2005 through August 31, 2006.

Preparation of Abstract

An abstract will be prepared for the 2006 Pittsburgh Coal Conference. The abstract will address specific results achieved as a result of research funded through the CBRC program.

Quarterly Newsletter, *Ashlines*

The Winter issue of *Ashlines* will be placed on the web page next quarter. E-mail notices will be sent to those on the CBRC *Ashlines* list serve.

Coal-Fired Co-Generation Facility Feasibility Study

The final report will be finalized and submitted to DOE-NETL.

EASTERN CENTER QUARTERLY PROGRESS REPORT

Submitted by: Jim Hower
Director, CBRC Eastern Regional Center

Tamara Vandivort - Re: CBRC Quarterly Reports Due Jan. 17

From: Jim Hower <hower@caer.uky.edu>
To: "Tamara Vandivort" <Tamara.Vandivort@mail.wvu.edu>
Date: 1/5/2006 3:02:44 PM
Subject: Re: CBRC Quarterly Reports Due Jan. 17

I continued to read the reports from the Eastern Region researchers and began the process of evaluating the current round of proposals.

At 02:23 PM 1/5/2006, you wrote:

> It's that time again, folks. I need your quarterly reports on your CBRC projects by January 17, 2006. Thx and let me know if you have any questions.
>
> Tamara Vandivort, Program Coordinator
> West Virginia Water Research Institute
> West Virginia University
> PO Box 6064
> Morgantown, WV 26506-6064
> (304) 293-2867 x 5448
> (304) 293-7822 Fax
> tvandivo@wvu.edu

Midwest Center Quarterly Progress Report

Submitted by: Yoginder P. Chugh
Director, CBRC Midwestern Regional Center

Combustion Byproducts Recycling Consortium (CBRC)
Midwestern Regional Center
Quarterly Progress Report October 1, 2005 – December 31, 2005

Submitted by
Yoginder P. Chugh
CBRC Midwestern Regional Center

On 1/10/06

Task Description

The Midwestern Regional Center (MRC) will perform two primary tasks:

1. Technical administration of CBRC projects in the Midwestern region, including
   - Participation in National CBRC steering meetings, conference calls, and other communications.
   - Facilitating communication within the region with the Regional Chair and Review Committees.
   - Facilitating the proposal submittal and review process.
   - Facilitating project activities and reporting and coordinating with the national CBRC office

2. Financial Administration of the research contracts awarded in the midwestern region during the first round regional and national competitions.

Accomplishments for the Period

1. Worked with researchers at SIU and ISGS to submit full proposals to National Center.
2. Continued to assist with utilization strategies for IGCC byproducts.
3. Assist with development of low permeability material for engineered caps and liners for mine reclamation.
4. Met with landfill owners from Chicago to demonstrate engineered soils for daily cover material.
5. Presented three papers at the International Fly Ash Congress in India, December 4-7, 2005.

Status of Ongoing Projects

- **ECM-07 "Industry – Government – University Cooperative Research Program for Development of CCBs-Based Light Poles For Electric Utility Industry," (Y.P. Chugh, Southern Illinois University)**

  Dr. Chugh met with Trinity Industries to determine if efforts to commercialize the project could be reopened. The Company has agreed to revisit the project. Additional meetings are planned in January 2006. In the mean time, the final report development continues to progress.

- **CBRC M-9 "Environmental Performance Evaluation of Filling and Reclaiming A Surface Coal Mine with Coal Combustion Byproducts," (Ish Murarka, ISH, Inc.)**

  The National Center has reached the PI. He has agreed to submit the final report within the next 30 days. This project is very important to the Midwestern Region and findings of the report will be disseminated as soon as the report has been reviewed.

- **CBRC M-04 "Crushed Aggregates from Class C Fly Ash," (Anil Misra, University of Missouri – Kansas City).**

  The PI has met all requirements of the contract. The report is currently under review through the National Center.

- **CBRC M-23 "Quantifying CCBs for Agricultural Land Application" (David Hassett, University of North Dakota)**

  The project continues to make good progress.

- **CBRC M-21 "The Impact of Adsorption on the Mobility of Arsenic and Selenium Leached from Coal Combustion Products" (Dr. Bradley Paul, Southern Illinois University)**

  Dr. Paul's quarterly report has not been received to date. He promised he will submit the final report at the end of October 2005. I have sent him an e-mail to determine the status of his final report.

- **02-CBRC-M12, "Manufacturing Fired Bricks with Class F Fly Ash from Illinois Basin coals", (Dr. Mei-In Melissa Chou, Illinois State geological Survey)**

  I talked to Dr Chou around the middle of December to see if I could visit her facilities and review the project. Since she was busy, she suggested that I do so in January. I plan to schedule a visit to the facility soon.

Plans for the Next Quarter

- Continue to provide technical and coordination support to different projects within the region.
- Continue to provide support to industrial groups in the region.

Western Center Quarterly Progress Report

Submitted by: Debra F. Pflughoeft-Hassett
Director, CBRC Western Regional Center

Combustion Byproducts Recycling Consortium (CBRC)
Western Regional Center
Quarterly Progress Report October 1 – December 31, 2005

Submitted by
Debra F. Pflughoeft-Hassett, Director
CBRC Western Regional Center

Task Description
The Energy & Environmental Research Center (EERC) will perform two primary tasks as the CBRC Western Regional Center:

1. Technical administration of CBRC projects in the Western Region, including:
   - Participating in national CBRC meetings, conference calls, and other communications.
   - Facilitating communication within the region with the Regional Chair and Review Committees.
   - Facilitating the proposal submittal and review process.
   - Facilitating project activities and reporting and coordinating with the national CBRC office.
2. Financial administration of the research contracts awarded in the western region during the first-round regional and national competition and review.

Accomplishments for the Quarter
A brief summary of the status of Western Region CBRC projects follows.

ECW05 "Promote Increased Use of Coal Combustion Products to State Regulators and Government Agencies," Ish, Inc.

The National CBRC office communicated a final report date of December 9, 2005. The report was not received at either the Western Regional or National CBRC offices; however, the PI contacted both the Western Region Director and Tamara Vandivort of the National Office to indicate the report should be finalized by mid-January. The Western Region CBRC office offered to assist the final report preparation by performing formatting and word processing. The report has not yet been received, so although the Western Region office expects to offer these services, the report submittal date will have to be postponed to 2 weeks after receipt at the Western Region office.

02-CBRC-W9 "Power Plant Combustion Byproducts for Improved Crop Productivity of Agricultural Soils," Agricultural Science Center at Farmington, New Mexico State University (NMSU)

Work reported in the last quarter continued in large part into this quarter, including processing of soil samples for salinity, pH, sodium adsorption ratio, and plant available essential elements and trace metals. Stem materials from two hybrid poplar container studies were processed for acid digestion for trace metal analysis. Soil samples from the Soil Column Study were acid-digested in preparation for metal analysis. Data were compiled for statistical analysis.

Western Region Directorate Administrative Activities
The Western Region Director received full proposals for review for the final review process. Reviews will be accomplished before the review deadline in January.

Technical Progress

ECW05 "Promote Increased Use of Coal Combustion Products to State Regulators and Government Agencies," Ish, Inc.

The draft final report continues to be in preparation. No quarterly is expected.

02-CBRC-W9 "Power Plant Combustion Byproducts for Improved Crop Productivity of Agricultural Soils," Agricultural Science Center at Farmington, NMSU

As noted last quarter, greenhouse studies were completed for two treatments. A third treatment based on plant available iron (Fe) contained within the fly ash was applied at an equivalent rate based on soil test results. A comparative study used a commercially available chelated iron applied at the recommended addition rate, and a control set of containers as prepared with no addition of iron.

Preliminary results on earlier container studies indicated benefits from the 20-T/acre-addition fly ash. Trace element analyses of the processed soil, leaf, and stem material from earlier tasks continued. Other analyses continued during the quarter included salinity (EC), sodium adsorption ratio (SAR), and pH.

Under the leachate column study, terminated in August 2005, 12 soil samples were retrieved by dissecting each column in 2.5-cm sections. Analysis of these samples was initiated in December.

Plans for the Next Quarter
The Western Region Director will finish reviews of the full proposals and attend the National Steering Committee meeting in January. Additionally, the Western Region Director will participate in discussions and prepare appropriate documentation to describe the success of the CBRC program, provide documentation on regional budgeting, and other activities to support activities of the CBRC directorate. It is anticipated that the final report for Western Region Project ECW05 entitled "Promote Increased Use of Coal Combustion Products to State Regulators and Government Agencies" will be completed and submitted in January.

Financial Information
A financial report is being submitted under separate cover.

Eastern Regional Projects
Active Projects:

01-CBRC-E10-Butalia
02-CBRC-E6-Herd

01-CBRC-E10

Full Scale Testing of Coal Combustion Product Pavement Sections Subjected to Repeated Wheel Loads

Dr. Tarunjit S. Butalia

01-CBRC-E10 Quarterly Report

Project Title: Full-Scale Testing of Coal Combustion Product Pavement Sections Subjected to Repeated Wheel Loads

Reporting Period: October 1, 2005 – December 31, 2005

Prepared by: Dr. Tarunjit S. Butalia (614-688-3408), The Ohio State University
Professor William E. Wolfe (614-292-0790), The Ohio State University

1. Introduction

The objective of this research project is to conduct accelerated load testing of full-scale pavements constructed of coal combustion products (CCPs) and compare their performance with sections constructed with conventional materials. As a part of the overall project, an innovative mechanics based approach will be developed for designing of pavements constructed of coal combustion products (CCPs). The pavement will be modeled as an elastic (or visco-elastic) mutli-layered system placed on an elastic (or visco-elastic) foundation. Resilient modulus testing will be carried out for cohesive and non-cohesive CCPs and soils, and granular materials to be used in the pavement system. The material property database information will be used as input to the finite element mutli-layered models to predict the stress, strain, and displacements at various points within or below the pavement structure. This will allow the research team to accurately model the response of the pavement when subjected to loading. The stress, strain, and displacement predictions from the mechanics model will be compared with the actual measurements made from the pavement sections (in year 2 and 3) subjected to accelerated loading at the OSU/OU Accelerated Pavement Load Facility in Lancaster, Ohio.

2. Task Description

Task 1: Develop innovative mechanics based approach
Task 2: Pavement modeling
Task 3: Resilient modulus laboratory testing
Task 4: Additional laboratory testing
Task 5: Develop material property database for CCP and natural materials
Task 6: Conduct existing empirical design
Task 7: Determine thickness of pavement layers and their constituents
Task 8: Comparison of mechanics based predictions with field observations

3. Summary of Period's Accomplishments & Significant Events

Analysis of data collected during loading of concrete and asphalt sections up to 20 years of State Highway traffic (135,000 cycles) was carried out. Laboratory samples collected during the construction of the full-scale pavement sections were tested in the laboratory and compared with design mix values. The pavements were saturated with water and the pavements were loaded for an additional 5 years of highway traffic. Pavement loading ended December 31, 2005.

4. *To Date Accomplishment*

	Completed
Task 1: Develop innovative mechanics based approach	75%
Task 2: Pavement modeling	80%
Task 3: Resilient modulus laboratory testing	90%
Task 4: Additional laboratory testing	75%
Task 5: Develop material property database for CCP and natural materials	75%
Task 6: Conduct existing empirical design	100%
Task 7: Determine thickness of pavement layers and their constituents	100%
Task 8: Comparison of mechanics based predictions with field observations	55%

5. *Technical Progress*

The technical data will be included in the final report

6. *Plans for Next Quarter*

The concrete and asphalt pavements (CCP and control sections) will be removed and samples will be obtained for laboratory testing. The development of the mechanics based theoretical model will be further refined with the additional monitoring data already collected on the pavement with freeze-thaw cycling and saturation of pavement layers.

7. *Financial Report to date*

Fund Source	Project budget	Expenditures to date	Expenditures as % of budget
CBRC	$70,000	$ 31,700	45.2%
OSU	$233,685	$ 540,422	231.2%
OCDO	$230,258	$ 751,776	326.4%
Total	$533,943	$1,323,898	247.9%

Prediction of the Effects of Placing CCBs in Contact with Mine Spoil

02-CBRC-E6

Richard Herd

Prediction of the Effects of Placing CCBs in Contact with Mine Spoil
CBRC Project 02-CBRC-E6

Combustion Byproducts Recycling Consortium
National Mine Reclamation Center
West Virginia University

Introduction

Uncertainty regarding the leachability and mobility of toxic ions from CCBs is the most significant deterrent to wide spread use of coal ash in large scale mine reclamation and other beneficial use projects.

The objective of this project is to determine if the mine water leaching procedure (MWLP) is effective in predicting the ability of mine spoil to retard toxic ion mobility at proposed CCB mine beneficial use sites. The secondary objective is to quantify the magnitude of retardation for various ions and to translate the results into protective recommendations for field deployment.

Five different treatment ratios of both CCB (class F) and FBC ash and neutral, non-pyritic mine spoil (sandstone and shale) will be subjected to MWLP in accordance with the protocol shown below and analyzed for trace elements, pH, alkalinity and acidity to determine leachable element adsorption to mine spoil.

Task Descriptions

Task 2. Conduct sequential leachings on CCB/spoil mixtures

The MWLP sequestial leachings of the fly ash/sandstone and fly ash/shale spoil mixtures in the variable combination ratios contained in the proposal were completed. Initial results were inconclusive therefore a new experimental design was devised (see below). The MWLP sequential leachings of the class F and FBC ash with both sandstone and shale at the new experimental ratios have been completed.

Task 3. Leachate collection and analysis

All leachate samples have been analyzed for pH, alkalinity, acidity, Ca, Mg, Fe, Al, Mn, Sb, As, B, Ba, Be, Cd, Cr, Pb, Hg, Se, Cu, Tl, Ag, Ni, V, Mo, and Zn.

Task 4. Data entry and analysis

All CCB/sandstone and CCB/shale spoil leachate results have been entered into an Excel spreadsheet. Data analysis is underway.

Summary of Accomplishments and significant events

The initial MWLP treatments of both sandstone and shale/CCB mixtures produced inconclusive results as presented in last quarters report. Based on these preliminary results the experimental design was modified in accordance with the spoil and CCB treatment mixture combinations as shown below:

MWLP All data are in grams

	Treatment				
	PCF/SS 1	PCF/SS 2	PCF/SS 3	PCF/SS 4	PCF/SS 5
class F	100	100	100	100	0
sandstone	0	25	50	75	100
total solids	100	125	150	175	100
AMD T&T	1000	1250	1500	1750	1000
solid/liquid	10%	10%	10%	10%	10%

	Treatment				
	PCF/SH 1	PCF/SH 2	PCF/SH 3	PCF/SH 4	PCF/SH 5
class F	100	100	100	100	0
shale	0	25	50	75	100
total solids	100	125	150	175	100
AMD T&T	1000	1250	1500	1750	1000
solid/liquid	10%	10%	10%	10%	10%

	Treatment				
	FBC/SS 1	FBC/SS 2	FBC/SS 3	FBC/SS 4	FBC/SS 5
FBC ash	100	100	100	100	0
sandstone	0	25	50	75	100
total solids	100	125	150	175	100
AMD T&T	1000	1250	1500	1750	1000
solid/liquid	10%	10%	10%	10%	10%

	Treatment				
	FBC/SH 1	FBC/SH 2	FBC/SH 3	FBC/SH 4	FBC/SH 5
FBC ash	100	100	100	100	0
shale	0	25	50	75	100
total solids	100	125	150	175	100
AMD T&T	1000	1250	1500	1750	1000
solid/liquid	10%	10%	10%	10%	10%

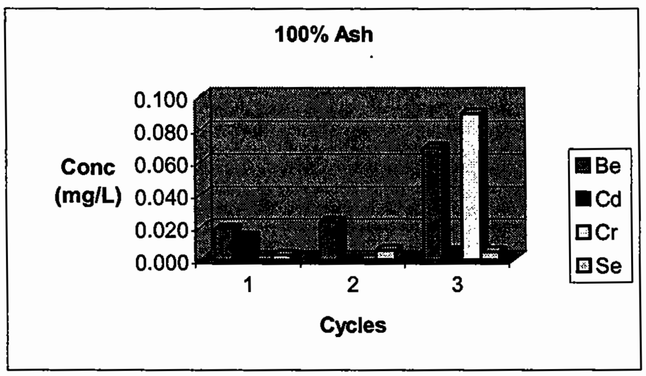
To-Date Accomplishments

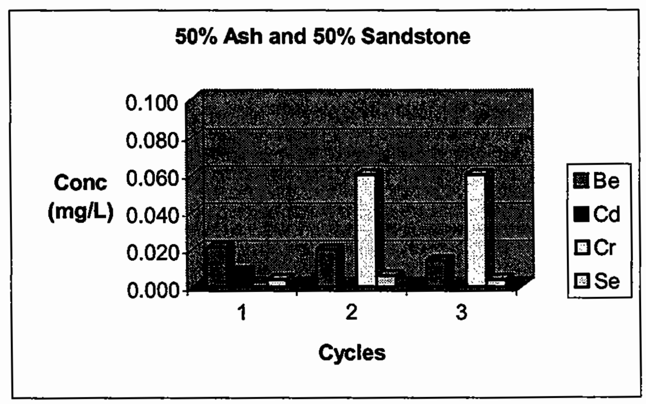
Based on the expanded experimental design, tasks 2, 3 and 4 are approximately 85% complete.

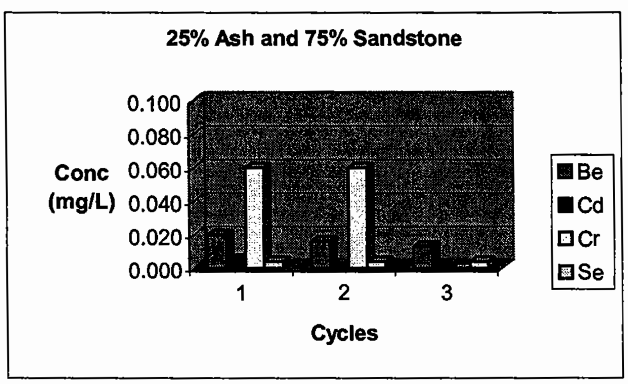
Technical Progress

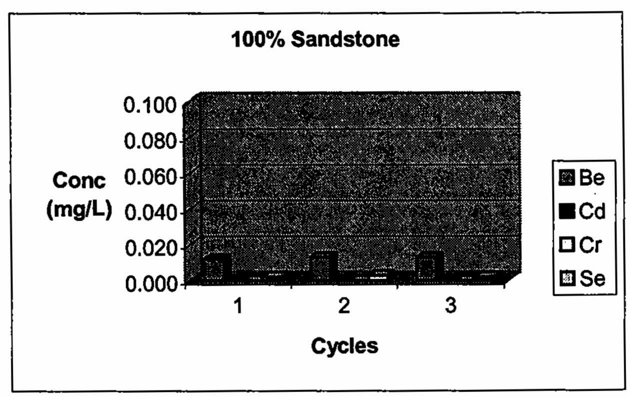
Initial MWLP sequential leaching results for the variable ratios of Class F ash and sandstone were reported in the July, 2005 report (reproduced below).

These graphs show preliminary fly ash/sandstone mixture MWLP leachate results for the trace elements beryllium, cadmium, chromium and selenium. Sandstone spoil appears to increase the rate at which chromium is leached. Both beryllium and cadmium had an affinity for adsorption by sandstone spoil. Selenium leachate concentrations remained relatively constantunder various treatment ratios of sandstone spoil indicating little if any adsorption activity. The leaching rate of arsenic copper, nickel and zinc present in fly ash did not appear to be influenced by addition of spoil material.









The variable nature of these results dictated a modification of the experimental design as shown above. The new design will maintain a constant (100g) amount of ash in each sequential leaching as opposed to varying the amount of ash and FBC as originally proposed.

Plans for Next Period
Data analysis will be completed and the final report compiled.

Financial Report
Expenditures = $ 56,204.30

Midwestern Regional Projects
Active Projects:

99-EC-M07 - Chugh
00-CBRC-M9 - Murarka
01-CBRC-M21 - Paul
01-CBRC-M23 - Hassett
02-CBRC-M12 - Chou

Industry-Government-University Cooperative Research Program for Development of Coal Combustion By-Products-Based Light Poles for Electric Utility Industry

99-EC-M07

Dr. Y. P. Chugh

QUARTERLY TECHNICAL REPORT
October 1, 2005 through December 31, 2005

Project Number: ECM07

Project Title: INDUSTRY-GOVERNMENT-UNIVERSITY COOPERATIVE RESEARCH PROGRAM FOR DEVELOPMENT OF COAL COMBUSTION BY-PRODUCTS-BASED LIGHT POLES FOR ELECTRIC UTILITY INDUSTRY

Principal Investigator: Dr. Y. P. Chugh

Other Investigator: Jinrong Ma, Department of Mining and Mineral Resources Engineering, Southern Illinois University at Carbondale

PROGRESS REPORT

1. During this period and again in January 2006, Dr. Chugh met with Trinity Industries to revisit the commercialization of utility poles by contacting the professionals at the corporate level. They have agreed to reopen the discussion. Additional meetings are planned during the present quarter.
2. Final report preparation for the project is progressing. The PI plans to submit the final report by May 15, 2006.
3. Mr. Jim Cutney, a consultant in Indiana, has indicated that there may be market for fly ash based poles in Gulf States area. The PI I working with him to convince Trinity Industries to see if they will fund capital for commercialization.
4. Mr. Ma successfully defended his dissertation on the research performed through this grant.

Environmental Performance Evaluation of Filling and Reclaiming a Surface Coal Mine with Combustion Products

00-CBRC-M09

Ishwar P. Murarka

Progress Report for the Three Quarters
From April 1, 2005 through December 31, 2005
For Subcontract No. 98-166-II
Environmental Performance Evaluation of Filling and Reclaiming a Surface Coal Mine with Coal Combustion Byproducts

P.I.: Ishwar P. Murarka
Ish Inc.

Introduction

This research project is carried out at the Universal Mine site in Indiana where CCBs from Wabash River Power Plant of Cinergy Corporation were used to fill the final surface coal mine pit. This surface mine pit was created by the coal mining operations by Peabody Mining Company. The research consists of both field and laboratory studies. The field studies involved installing several ground water monitoring wells on the south side of the property and collecting data on the groundwater flow, groundwater quality, and surface water quality in a spatial and temporal manner. Nine temporal sampling and analysis of research wells has been completed during the period spanning from May 2001 through October 2005 of this research project. The last semi-annual monitoring (as part of the third year funded study) of the research wells and surface water locations was carried out in the third quarter of 2005 to provide data for a long-term assessment of water quality conditions and the fate of leachate constituents derived from the CCB placed in the open pit mine at the Universal Site. The water quality and hydrology data will be analyzed during February through March 2006 of this project statistically, mathematically, graphically, and by geochemical methods as appropriate to prepare and submit the draft report on the project by the end of March 2006.

A Ph.D. student at Purdue University has been carrying out the laboratory batch and column studies. Both fresh and aged CCB samples from the power plant and the site as well as the mine spoil material from the site were utilized to conduct batch and column experiments to develop the scientific understanding of leaching and attenuation of selected constituents. Arsenic species and boron are the target chemicals for the attenuation research. Papers have been and will be prepared for presentation at conferences and publications in the open literature as appropriate.

The PI will participate in technical meetings and in technology transfer efforts to disseminate the results of this research.

Task Description

Task 1 pertains to obtaining and synthesizing historical monitoring data on hydrology, groundwater quality, surface water quality, ash bulk composition, and laboratory generated ash leachates. The quarterly compliance monitoring at the Universal site by Cinergy (formerly PSI) began in 1988 and has continued without any interruption through calendar year 2005. During 2001, research-monitoring wells were installed and are being monitored on a quarterly basis with a gap of two quarters in 2002 because of delays in receiving the second year of CBRC funds. Quarterly monitoring of the research wells and surface water sampling locations resumed in the 4th quarter of 2002 with the CBRC/Cinergy/EPRI/Ish Inc. funding allowing sampling and analysis effort through the 3rd quarter of 2003. Third year funding request was approved by the CBRC and the other cofunders so that groundwater monitoring can be carried out on a semi-annual basis for one more year spanning through the third quarter of 2005. The third year funding also allowed us to extend the laboratory column tests to assess the long term leaching and attenuation characteristics of selected ash constituents particularly arsenic and boron. The 3rd year CBRC funding was released in October 2004 and we accordingly collected the last round of groundwater sampling for the research project in the third quarter of 2005. The last round of compliance monitoring by Cinergy occurred in the fourth quarter of 2005.

Task 2 involved designing and installing approximately 16 monitoring wells to obtain spatial distribution of groundwater quality downgradient of the CCB fill area. The field effort also obtained core samples from ash and overburden materials from the site to conduct laboratory experiments. Field measurements were made to obtain the physical properties of the porous media and to establish the groundwater flow field. Water levels and other hydraulic parameters, as needed, were monitored.

Task 3 consisted of carrying out sampling and analysis for groundwater quality from the research wells on seven occasions during the first and second years of the CBRC funded research period ending in March 2004. As a result of the 3rd year funding for the project two more rounds of sampling and analysis of groundwater and surface water were completed in 2005. Cinergy has been collecting and providing comprehensive monitoring data for groundwater quality from the compliance monitoring wells for twenty quarters for the period beginning in January 2001 and ending in December 2005. In addition, approximately six surface water locations were also monitored for water quality by Cinergy. Acid-base accounting, effects of pH and Eh changes on the leaching and mobility of selected constituents will be examined to some extent. Attenuation chemistry and the responsible geochemical reactions will also be studied mostly for arsenic and boron. Both concentrations and mass calculations will be carried out to analyze the monitoring data. Groundwater transport and fate model(s) will be used, as needed, to assess the groundwater monitoring data for migration and attenuation of selected ash constituents.

Task 4 comprised of conducting laboratory experiments using geological material from several core samples obtained from the site. Sequential leaching tests and equilibrium partitioning tests will be carried out for a selected set of soil samples and ash constituents. Column experiments were designed and conducted to develop a combined understanding of release and attenuation of arsenic species and boron as part of the second and third year research.

Task 5 involves preparing and submitting papers for publication and carrying out technology transfer functions. A comprehensive draft report for the research project will be prepared and submitted to project funders at the end of the third year of the project in March 2006. Overall project management and coordination of research amongst various investigators will be carried out under this task by the PI. All preparations of progress reports, participation in technical meetings and presentations at conferences/symposiums will be carried out under this task.

Summary of Accomplishments and Significant Events

As part of Task 1, we have completed collecting and adding all new monitoring data from the research wells and surface water locations through the end of the third quarter 2005 to the MANAGES database. The first three quarters of the compliance monitoring data for the year 2005 collected by Cinergy were also received, fully checked and incorporated into the MANAGES database during March through November 2005 time period. Both research and compliance water quality data for groundwater, surface water and ash leachates have been fully validated and the MANAGES database is now complete through the third quarter of the calendar year 2005. The fourth quarter 2005 of compliance monitoring data are being validated and incorporated in the MANAGES database before the comprehensive analyses and report preparation efforts are completed in February and March 2006.

Task 2 was completed and all monitoring wells were installed and developed for the research purpose in calendar year 2001. Measurement of hydraulic properties and water levels have been performed and additional water level data will be collected when quarterly water quality monitoring samples are collected through the remaining period of performance for this research project.

As part of Task 3 effort, all data through the 3rd quarter of 2005 from the research and compliance monitoring efforts have undergone QA/QC checks and the data validation work has been completed. Cation-anion balances were calculated for the compliance monitoring data and were found to indicate that the monitoring data continues to be of very good quality. The validated monitoring data through the third quarter 2005 were incorporated in the MANAGES database. The water samples for the compliance monitoring program were collected in mid-October for the 4th quarter 2005. Compliance monitoring data for the 4th quarter of 2005 has been just received and are undergoing checking for incorporation in the database in February 2006.

Figure 1 shows the map of the Universal site containing all monitoring locations. This figure also shows the AA' transact starting at the background monitoring well CB-9, traversing via CB-1S/CB-1D, CB-11, CB-10, CB-4, CB-11S/CB-11D, CB-13, and ending at CB-3/CB-7. The linear distances of the monitoring wells from CB-9 minus 300 feet and another 100 feet from CB1S/CB1D have been used to prepare these plots. Table 1 provides the distances and the corresponding monitoring well designations. Figures 2, 3, 4, 5 and 6 show the time series plots for boron, sulfate, calcium, arsenic and pH for the leachate monitoring wells at the Universal site.

These plots show that calcium, boron, and sulfate are all present in the ash leachate wells CB-1S/CB-1D and MW-8. These plots also show that the leachate concentrations in the ash in the former mine pit are essentially the same throughout the years of monitoring although there are some differences in the spatial locations. A preliminary interpretation suggests that Boron in the ash leachate is present in several mg/L concentrations (Figure 2)

The sulfate (Figure 3) concentration distribution data suggests that the ash produces elevated levels of sulfate in the leachate at the Universal site. These time-series plots further suggest that there is a steady state in leachate quality with respect to sulfate. The calcium (Figure 4) concentration data also suggests that the ash leaches calcium and has nearly a constant level of calcium present in the leachate at the field scale. The arsenic concentrations data are shown in Figure 5. This plot shows spatial variability in arsenic concentrations within the ash fill whereas the arsenic concentration at a given spatial location is nearly constant over time. Figure 6 shows that the pH of the ash leachate is alkaline in the range of about 9.

As part of Task 4, the graduate student at Purdue University has completed the column experiments during this reporting period to obtain data on the attenuation and breakthrough of arsenic species and boron under dynamic leachate flow conditions. One set of column results are shown in the figures 7 through 10 for the arsenic species and boron alongwith effluent pH and pore water velocity.

During the second quarter of 2003, we collected and analyzed a number of water samples from Universal site wells for As (III), As (V), MMA, and DMA. The arsenic species were measured using HPLC and ICP/MS equipments at the Illinois Hazardous Waste Research Center. The arsenic speciation results are shown in Table 2. These results indicate that both As(III) and As(V) species are present in the ash leachates as well as in groundwater wells that contain at least 5 ug/L of total arsenic. The leachate well MW-8 contains about 55% As(V) whereas the leachate well CB-1D contains about 90% As(V) species suggesting that there is spatial variability in arsenic species distribution in the ash leachate wells at the Universal site. The groundwater wells and the mine seep on the other hand contain between 25 to 30% As(V) indicating that As(III) is the prevalent species in groundwater downgradient of the Ash fill.

As part of the field and analytical work groundwater, surface water and leachate water samples were collected and analyzed for isotopic composition for Boron, Sulfur, Strontium, Hydrogen and oxygen during the third and fourth quarters of 2005. Table 3 contains preliminary summary of Boron isotopes results. All isotopic data will be evaluated and interpreted as we begin our data analyses and report writing efforts.

As part of Task 5, we will be evaluating the groundwater and the surface water monitoring data from the research and the compliance monitoring locations collected from 1988 through 2005.

The PI prepared a power point presentation on the Universal Ash Site research and delivered to the audience at the World of Coal Ash Conference in Kentucky in 2005.

The PI continues to provide the day-to-day project management functions and continues to design and direct the research as well as analyze data and interpret results as they were developed.

Plans for Next Period:

From January through March 2006 we plan to complete data analyses, prepare tables and figures, and prepare a draft of the comprehensive final report for the Universal Ash site. Summary statistics and trends analyses will be carried out as needed. Hydrologic evaluations and transport and fate modeling will be carried out as needed to prepare the report.

Invoicing and Financial Information:

During the last three quarters of 2005 (i.e. from April 1 through December 2005), Ish Inc. has incurred a total of about $51,730 in the research project related expenses. Approximately $28,451 will be invoiced to the University of West Virginia and the rest for the funds will be provided by the cofunders (i.e. Cinergy, EPRI and Ish Inc.)

Table 1 Distances and monitoring wells identity along transact AA'

Distance from CB-9 (ft)	Distance for Plotting Used (ft)	Monitoring Well ID
319	19	CB-1S
323	23	CB-1D
487	87	CB-11
543	143	CB-10
636	236	CB-4
728	328	CB-12S
732	332	CB-12D
918	518	CB-13
1094	694	CB-3
1094	694	CB-7

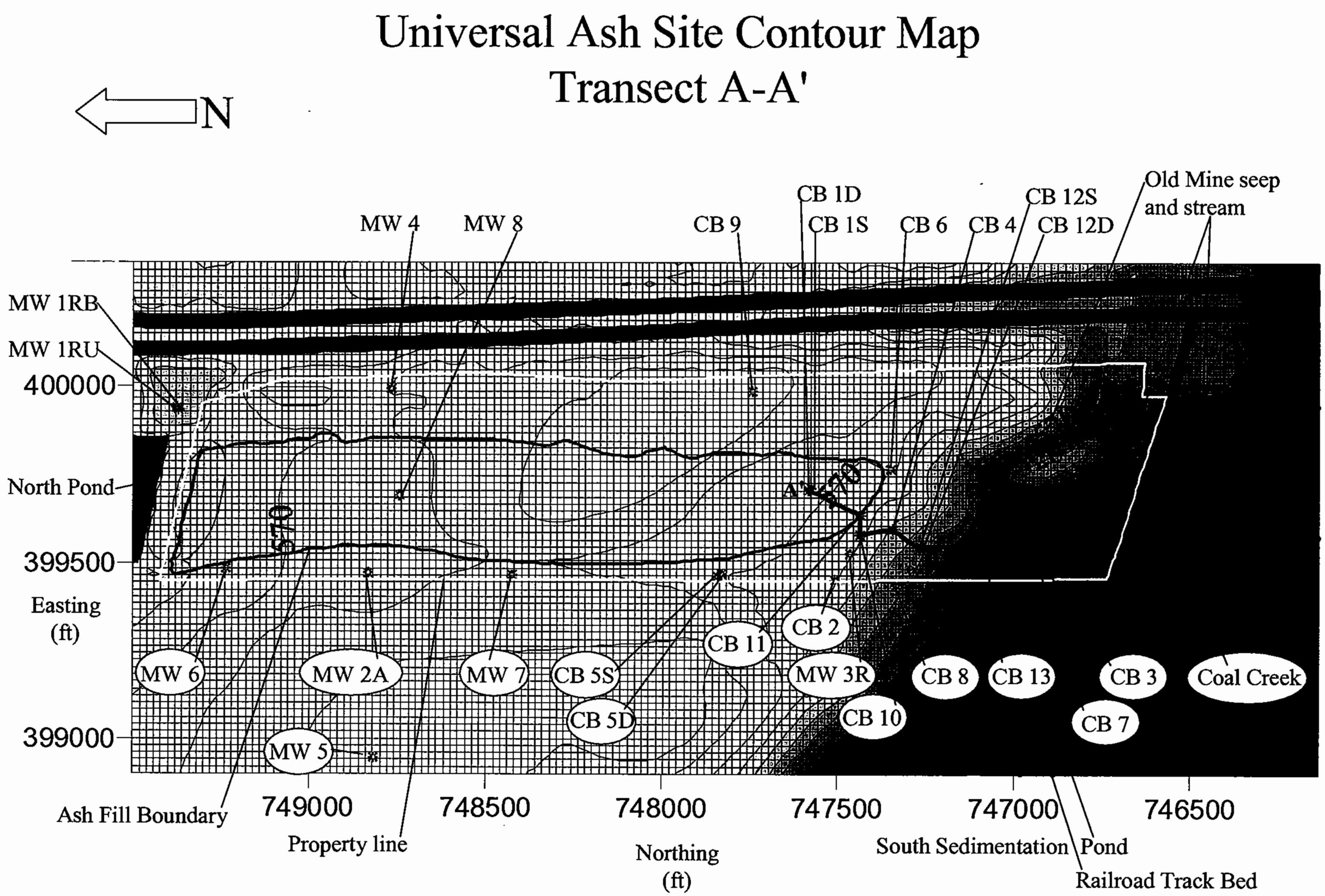
Table 2 Arsenic speciation results for groundwater and ash leachate samples obtained from the Universal Ash site during sampling in May 2003.

	Measured Concentrations in ug/L of				
Well ID	**As(III)**	**As(V)**	**MMA**	**DMA**	**Total As**
Leachate wells					
MW-8	98	127	<5	<10	216
CB-1S	3	2	<1	<1	<6
CB-1D	8	78	1	2	95
Groundwater wells					
MW-3R	3	1	<1	<1	5
CB-6	6	3	<1	<1	10
MW-1RB	6	4	<1	<1	11
CB-12S	17	7	<1	<2	22
Mine Seep 2	9	3	<1	<1	15

Table 3 Boron Isotopes Results for Groundwater, Leachate and Surface water samples from the Universal Site

Sampling Location	delta ^{11}B(‰)
CB 9	18.5
CB 10	19.9
CB 11	4.7
CB12D	38.7
CB 13	26.5
MW1RU	6.1
MW1RB	9.5
MW3R	28
MW4	20.7
MW8	5.7
Plug Seep	7.7
Mine Seep 2	16.3
CB 1S	6.6
CB 1D	2.9
CB 2	27.3
CB 4	33.8
CB 5S	25.2
CB 5D	27.2
CB 6	19.9

Figure 1 Monitoring locations for the research and compliance sampling points



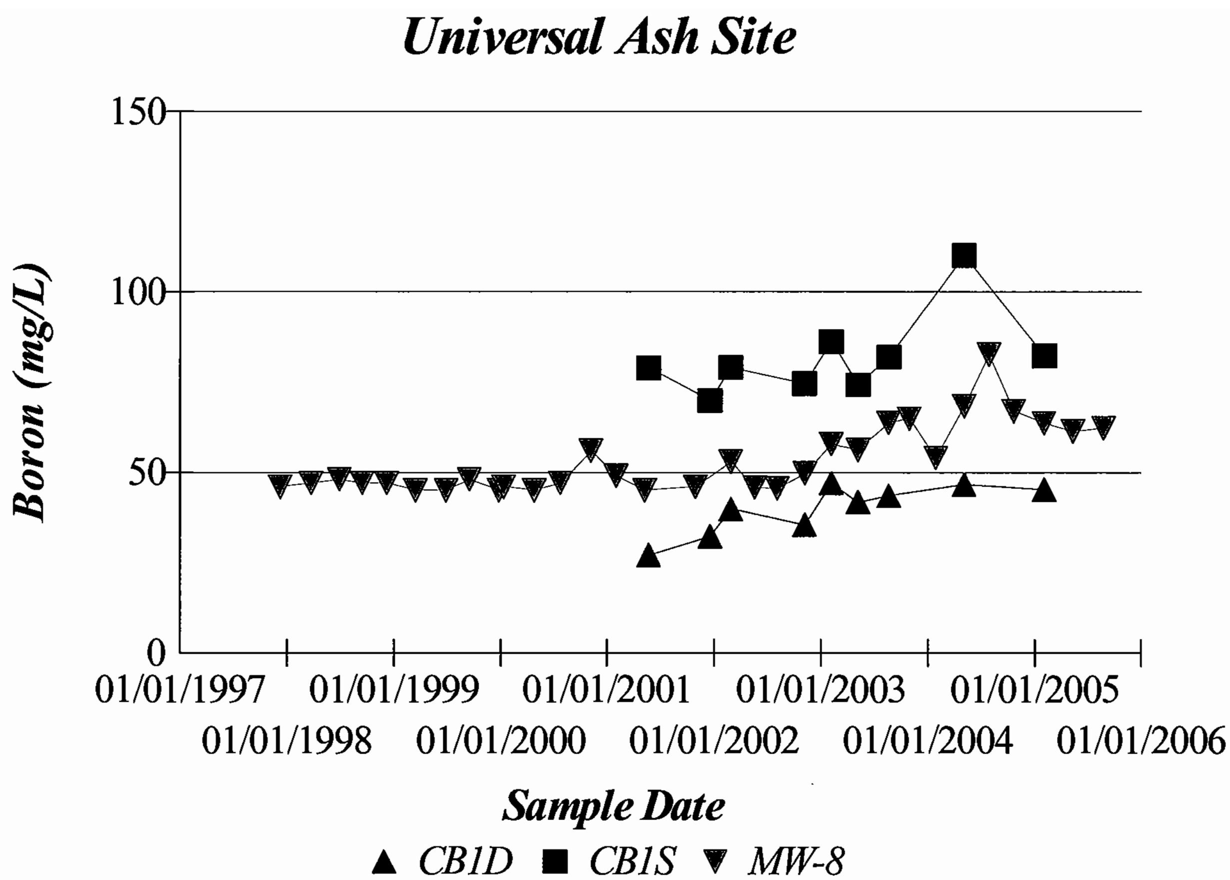


Figure 2: Time series plot for measured boron concentrations in leachate wells

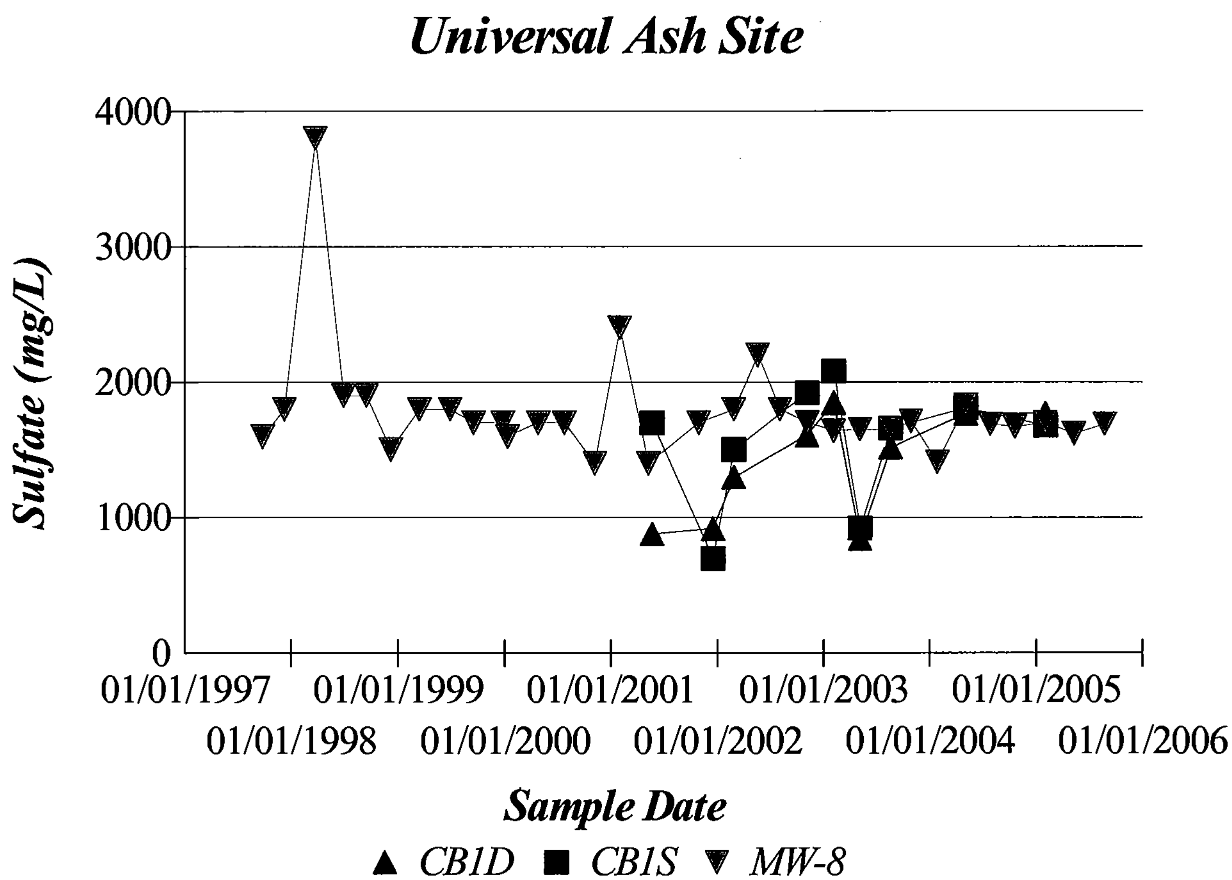


Figure 3 Time series plot of sulfate concentrations measured in the leachate wells

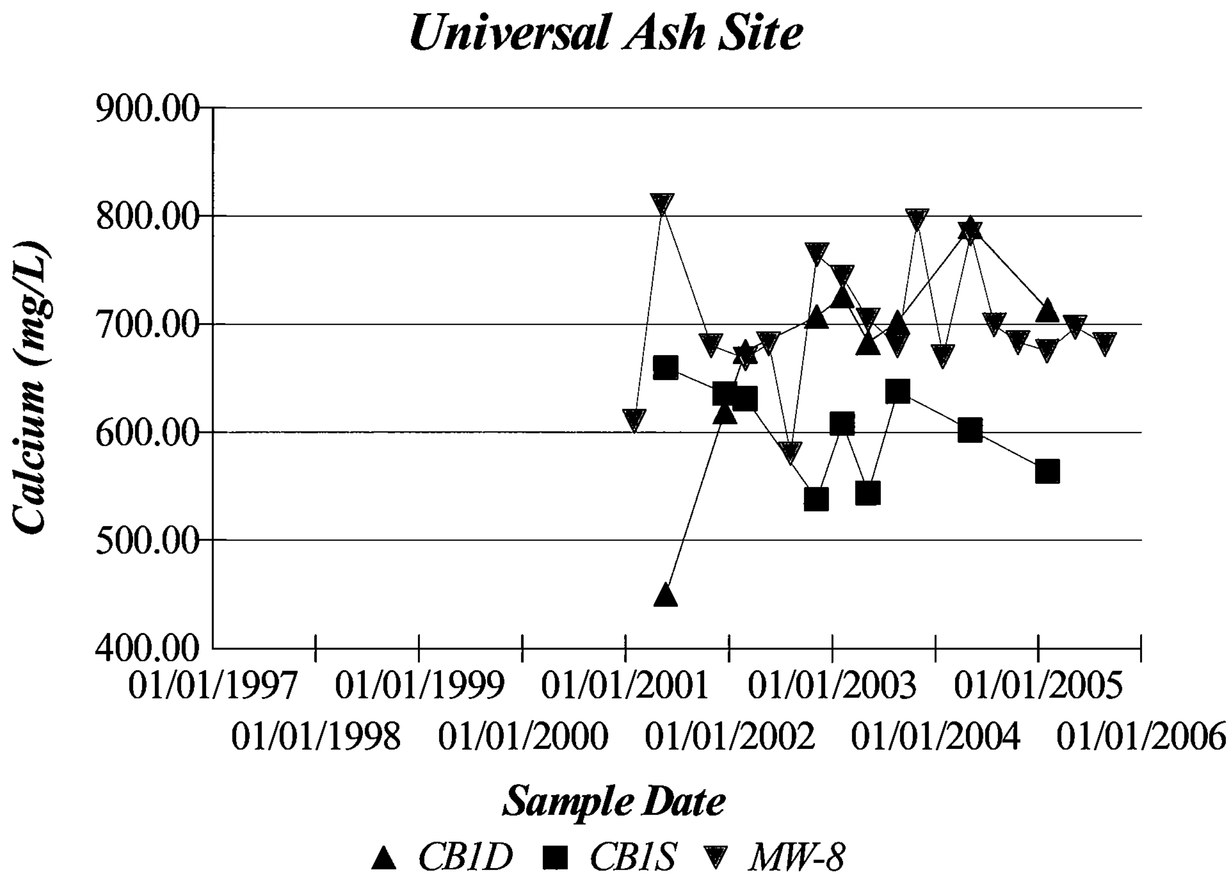


Figure 4 Time series plot of the measured calcium concentrations in leachate wells

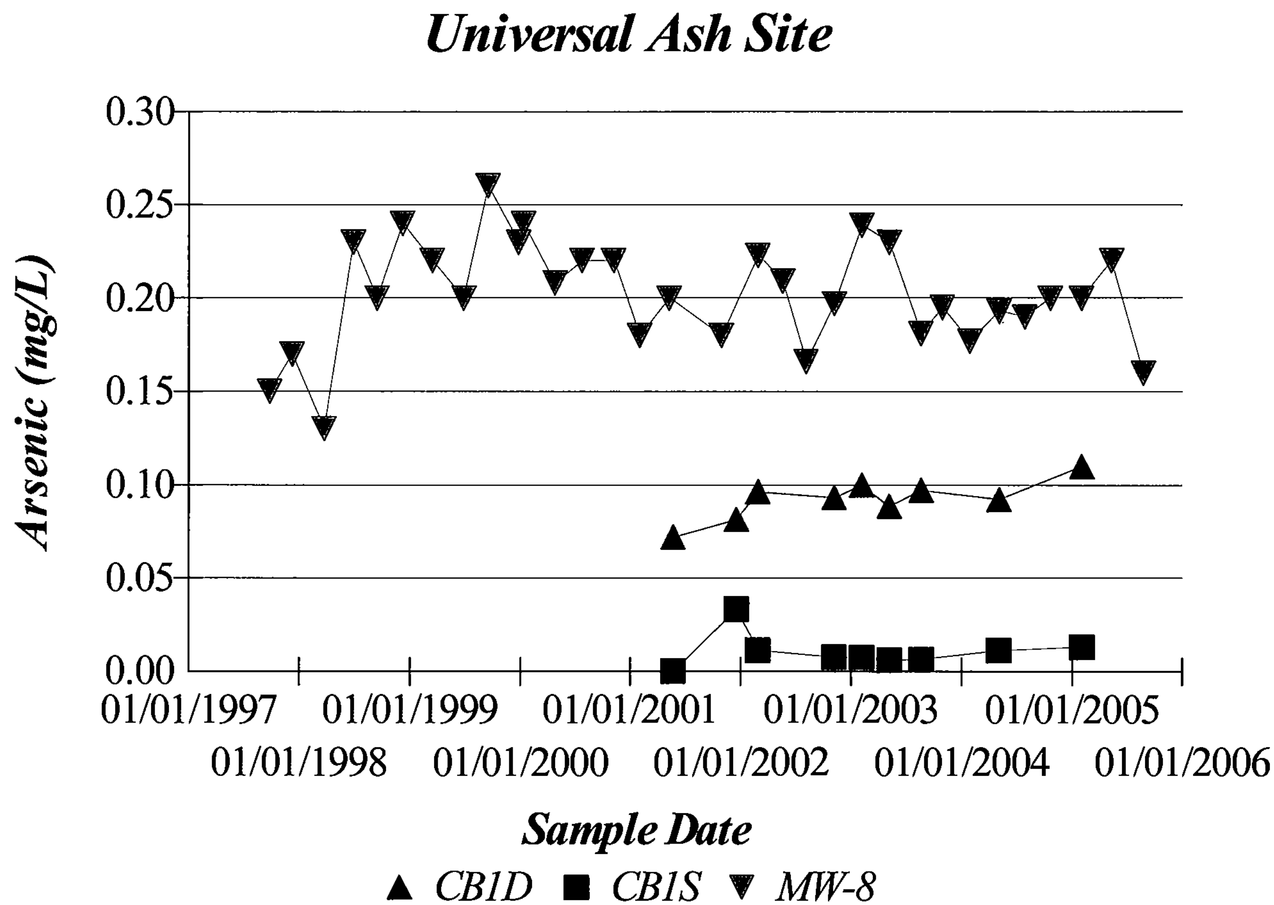


Figure 5 Time series plot for the measured concentrations of arsenic in leachate wells

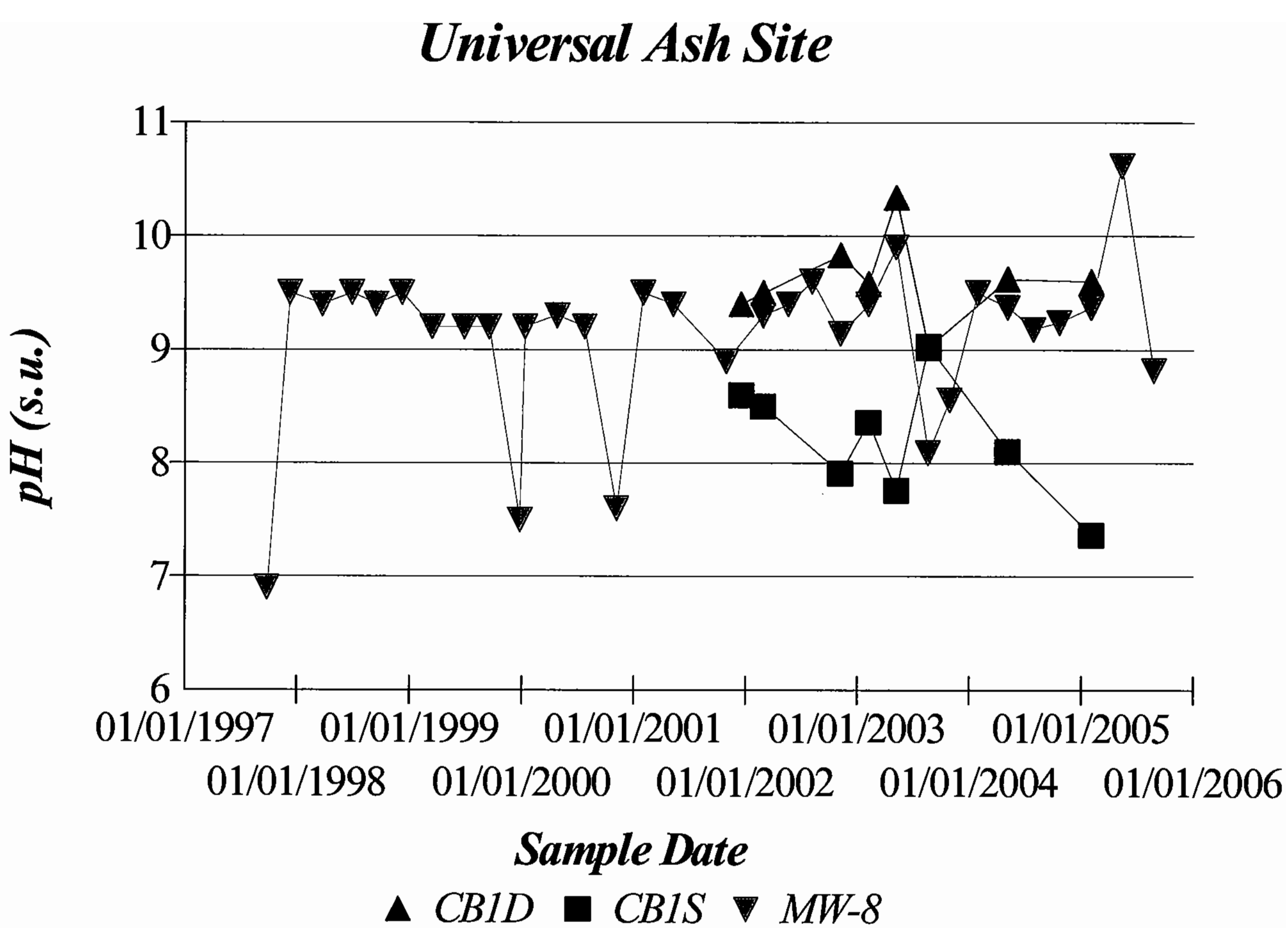


Figure 6 Measured pH of water in leachate wells.

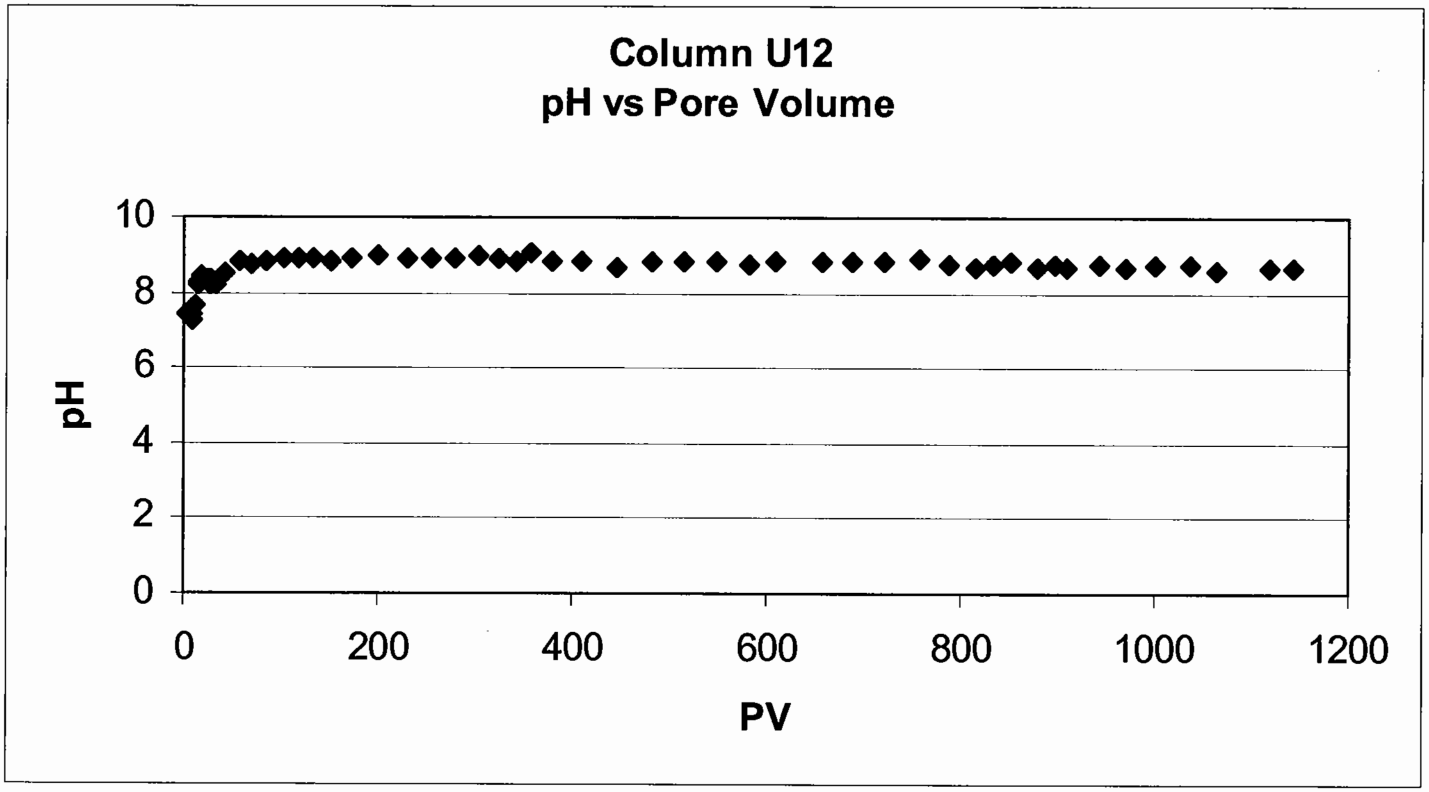


Figure 7 pH values measured in the laboratory Column effluent

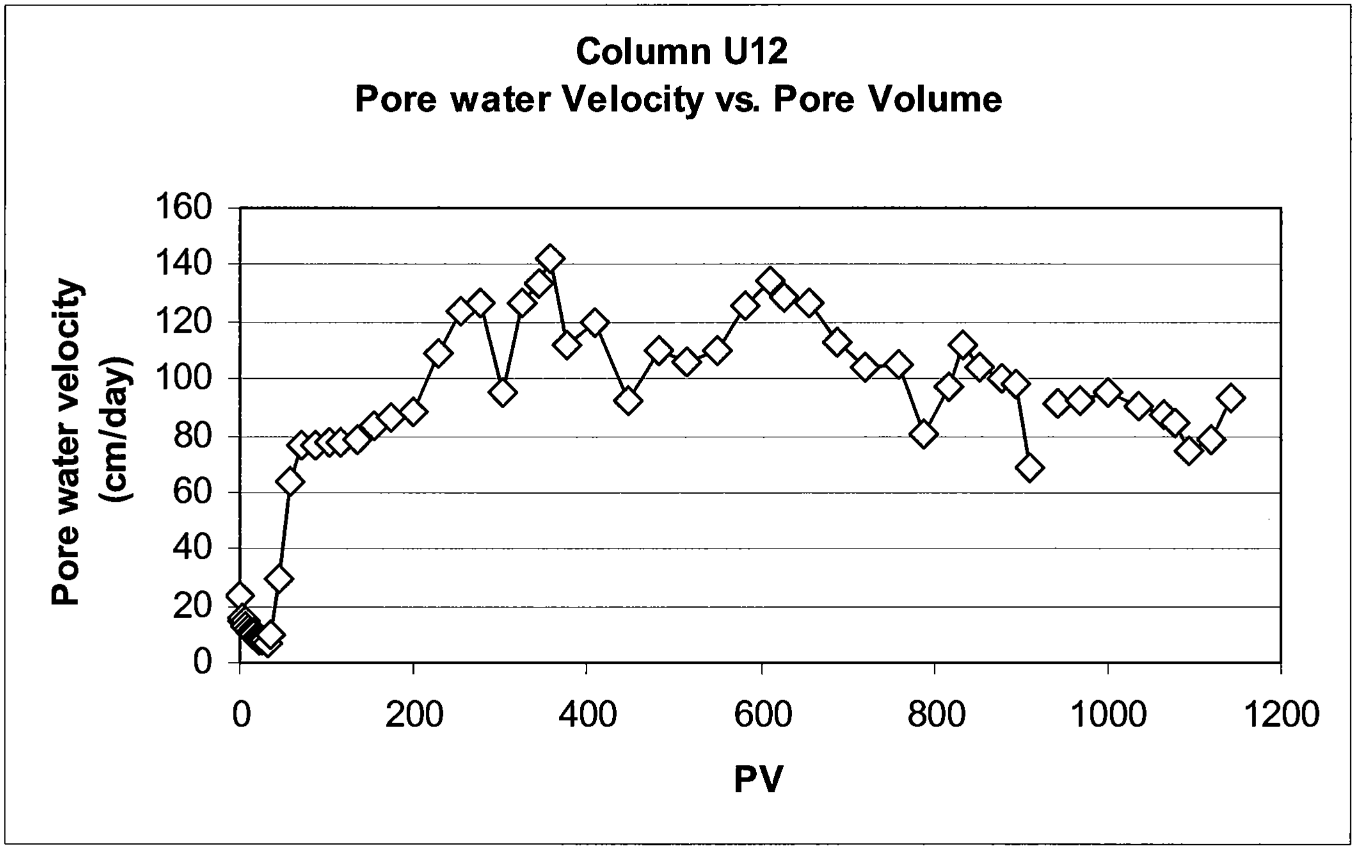


Figure 8: Pore water velocity as a function of pore volumes of water passed through the column

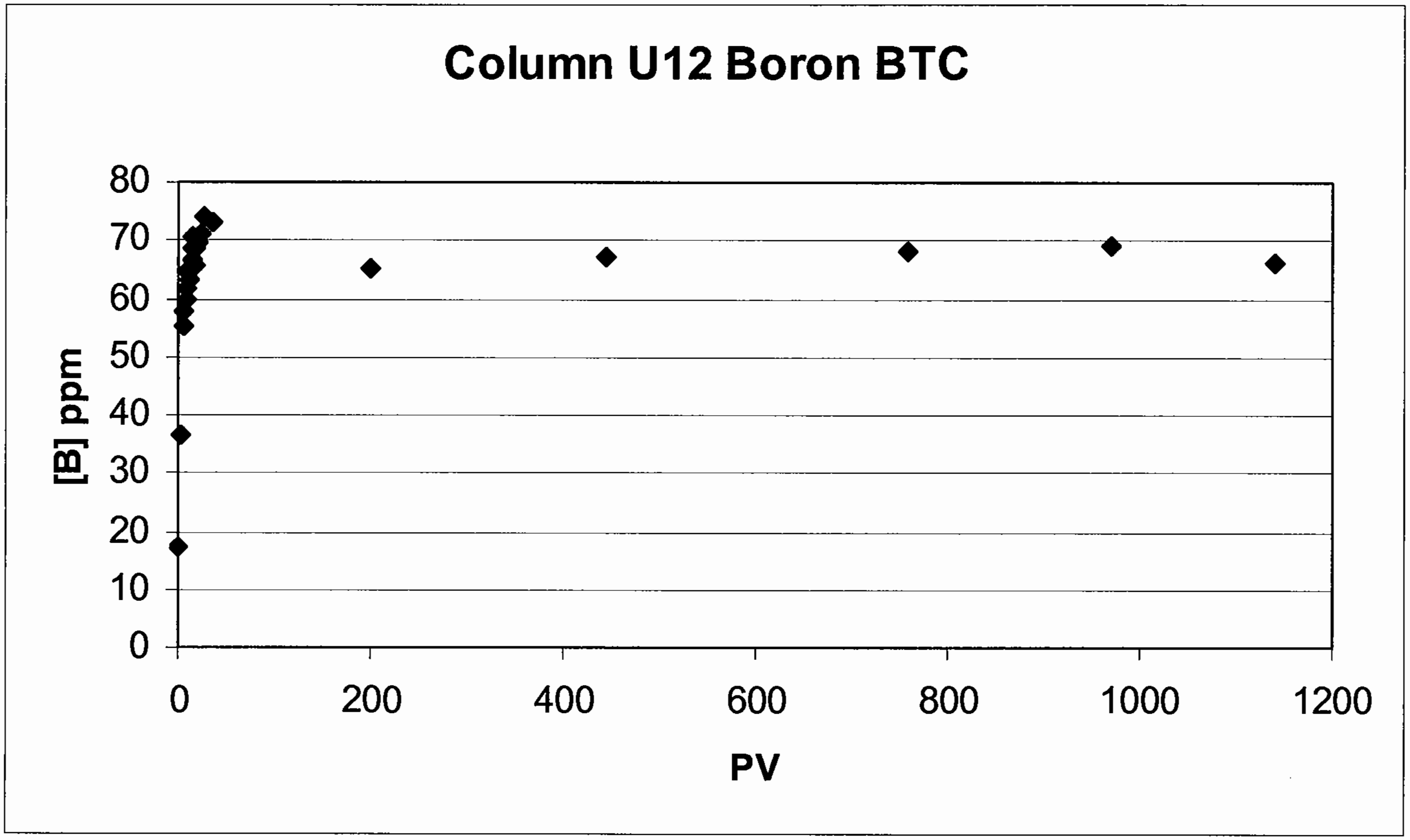


Figure 9 Breakthrough of Boron concentrations from the column

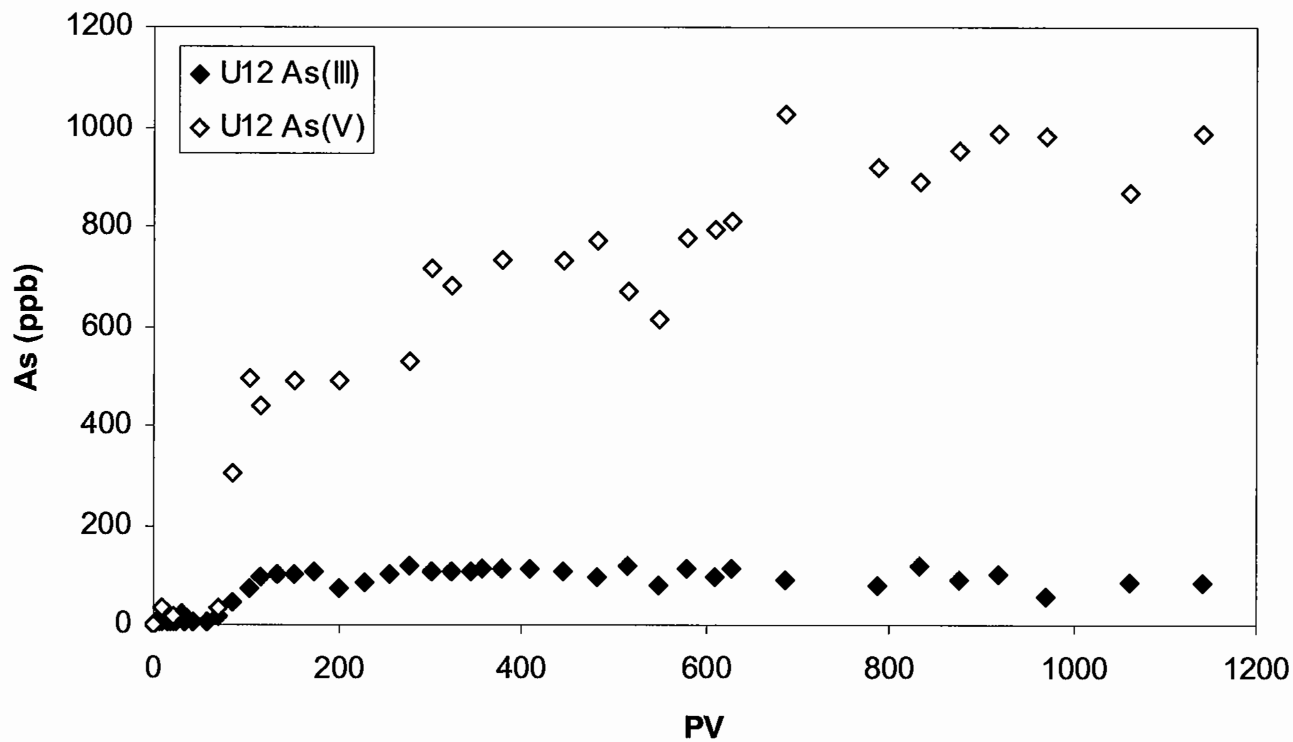


Figure 10 Breakthrough of arsenic species from the column packed with the spoil material

The Impact of Absorption on the Mobility of Arsenic and Selenium Leached from Coal Combustion Products

01-CBRC-M21

Dr. B.C. Paul

The Impact of Adsorption on the Mobility of Arsenic and Selenium Leached from Coal Combustion Products
(Time Period Oct 2005 to Dec 2005)

CBRC Project No.: 0-1-CBRC-M21

P.I.- Dr. B. C. Paul

Introduction

Regulatory frameworks effect the disposal and beneficial use of coal combustion products. Regulatory structures put in place for disposal often impact the perception of risk in beneficial use projects. Regulatory structures placed to "protect" the public during disposal encourage parallel regulations for beneficial use projects that will steer potential customers clear of recycling of combustion products in favor of less restrictive virgin materials.

Most fears about coal combustion products center on a belief that trace elements present in coal combustion products (and in fact naturally occurring rock in general) will leach into the groundwater supply where they will become a danger to public and environmental health. That trace elements are present in coal combustion products or that the can be leached is not a real question since water can leach trace elements from almost anything. The focus of this project is that environmental and public health risks that are based only on the presence of leachable trace elements will probably be overstated because the mere fact that something enters the water supply is no guarantee that it will remain there. Many of the trace elements in coal and consequently the ash that remains originated by water borne trace elements being adsorbed by clays or organic materials in ancient swamps. These same adsorption processes are active today and may remove trace elements from solution before they can be transported or dispersed any distance in the groundwater supply. Indeed EPA has developed standard methodologies for determining the amount of trace element adsorption that can be expected by soils, clays and other natural strata materials. Where this methodology was applied to boron using mine and road cut spoils and soils the results showed that only very small boron leachate plumes extending a few hundred feet could ever develop. This is in contrast to very large plumes extending for miles being predicted by models that failed to consider the existence of adsorption. While boron lacks the low level toxicity of arsenic and selenium this work expected and found much stronger adsorption of arsenic and selenium.

This project measured the adsorption of arsenic and selenium by soil and spoil material and examined the impact to be anticipated in terms of toxic plumes forming from coal combustion products contacting ground water. The results to be reported will go directly to the question of whether trace element exposure risks from combustion product leaching are accurately reported or overstated.

Task Description

The project involves 9 task steps.

Task #1 – With consultation from the advisory board select the samples to be studied for their adsorption properties.

Task #2 – Collection of samples chosen by the advisory board but not already available.

Task #3- Sample preparation.

Task #4 – Test concentrations of Arsenic and Selenium will be determined in cooperation with the Industrial Advisory Board.

Task #5 – Running the actual test batteries.

Task #6 – Running Analysis.

Task #7 – Running basic modeling.

Task #8- Feed back and reporting.

Task #9- Conference Reporting.

Efforts this past quarter have been in concluding the final report and defending the Ph.D. dissertation resulting from this work.

Summary of this Quarters Accomplishments and Significant Events

Mr. Shaui Chen defended his dissertation for his Ph.D. in October. The dissertation is based on this CBRC project. The work was approved by the committee and the thesis was approved subject to editorial changes. A condensed final report was prepared although obviously the dissertation is a much more extensive document.

To Date Accomplishments

The work on this project has been completed and final report arrangements are being coordinated.

Technical Progress

The work is complete.

Plans for Next Period

The dissertation should be finished. The Ph.D. degree should be awarded in May. Submission of the final report will be completed.

Qualifying CCBs for Agricultural Land Application

01-CBRC-M23

David J. Hassett

Qualifying CCBs for Agricultural Land Application
01-CBCR-M23
October 1 – December 31, 2006

Introduction

Agricultural application is one of the largest potential unrealized uses for coal combustion by-products (CCBs). This project will determine the appropriateness of mixed CCBs (bottom and fly ash and flue gas desulfurization [FGD] material) recovered from wet storage for agricultural land application. The CCBs reclaimed from disposal, individual ash samples before wet storage, untreated and field-treated soil samples, and Duck Creek Power Station ash pond water will be evaluated in a laboratory setting. A specified mixed ash will be evaluated, but the project is directed at developing and testing a process of qualifying ash for use as an agricultural soil amendment that will be broadly applicable.

Task Description

Task 1. Review of Existing Information

This task consists of obtaining and assembling all existing information on AmerenCILCO Duck Creek Station CCBs. Information on Illinois regulations concerning CCBs will also be obtained. This information will aid in directing the remaining research effort. Much of this information is already in the possession of Energy & Environmental Research Center (EERC) research staff.

Task 2. Sampling

Duck Creek Station personnel will obtain both solid and liquid samples. Solid samples will include soil, fly ash, bottom ash, FGD material, and as-managed CCBs. Two samples each of treated and untreated soil will be collected during the project. One sample each of fly ash, bottom ash, and FGD material will be collected in locations before entry to the wet disposal pond. Three samples of as-managed CCBs as well as one sample of pond water will be collected. Guidance for sampling protocols will be provided by EERC researchers.

Task 3. Laboratory Analysis

Solid materials will have major, minor, and trace constituents determined. Major and minor constituents include silicon, aluminum, iron, calcium, magnesium, sodium, potassium, titanium, manganese, phosphorus, strontium, barium, and sulfur and loss on ignition. A list of trace elements of concern will be developed and will include, but not be limited to, antimony, arsenic, boron, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium, thallium, and zinc. In addition to these 13 trace elements, up to four additional elements may be added based on a proton-induced x-ray emission analysis, which determines the elements from sodium through uranium. Sulfite/sulfate ratios will be done because of phytotoxicity.

Additionally, limited work on oxidation rates of sulfite will be performed. The solid samples will consist of one fly ash, one bottom ash, one scrubber sludge, two treated soil, two untreated soil, and three as-managed CCB samples.

Solid samples will be leached for 18 hours using the synthetic groundwater leaching procedure (SGLP). The samples subjected to leaching will be the three as-managed CCBs and the four soil samples. The resulting leachate liquids as well as collected ash pond water will be analyzed for the same parameters as the solid samples.

Task 4. Data Interpretation

Using the information collected in Task 1, a list of appropriate limits for analytical parameters will be developed. Application practices and rates will be determined and summarized. Beneficial properties of the ash will be identified. Results from Task 3 will be compared to these.

Task 5. Reporting and Technology Transfer

Project reporting will include required quarterly progress and financial reports. A comprehensive final report as well as a write-up for a CBRC newsletter will also be completed. The key deliverables for this effort will be:

1) A report to the Illinois Environmental Protection Agency (IEPA) facilitating its determination on the appropriateness of AmerenCILCO Duck Creek Power Station mixed ash for agricultural application in Illinois.

2) A generic document detailing the process for qualifying CCBs for agricultural application.

Summary of This Quarter's Accomplishments and Significant Events

Data interpretation and reporting efforts continued. A draft of the report for the IEPA was sent to Ameren for review.

To-Date Accomplishments

Task 1 is 100% complete.
Task 2 is 100% complete.
Task 3 is 100% complete.
Task 4 is 100% complete.
Task 5 is 15% complete.

Plans for Next Period

Report writing will be completed. The final report will be submitted.

Manufacturing Fired Bricks with Class F Fly Ash from Illinois Basin Coals

02-CBRC-M12

Melissa Chou

Tamara Vandivort

From: "Chou, Melissa" <chou@isgs.uiuc.edu>
To: "Tamara Vandivort" <Tamara.Vandivort@mail.wvu.edu>
Date: 1/9/2006 11:26 AM

Hi Tammy,

During my trip to India, I enjoyed the nice and warm weather over there. I also enjoyed their food and have learned several authentic dishes. Overall, my trip went smoothly, except for one road bump during my return at Chicago O'HARE. My connection flight at O'HARE airport to Champaign was cancelled one by one due to bad weather and I had to stay overnight for the next morning flight. But, the next morning flight was also cancelled. Finally, I couldn't wait any longer, and have Joe Chou came to give me a ride back to Champaign. My baggage was also misplaced.

It was a nice meeting. My talk went very well and was well received. In India, the government mandated that manufacturers have to include 30% of their local fly ash into their productions, such as brick or concrete products. In India, they use mold-pressed method for making bricks (unlike in the USA, more than 95% of the manufacturers use an extrusion method). I received many requests. For example, I separately met with a group from one organization. They showed me their test results, and told me during testing, after they had the mold removed, the material was falling apart, and asked what they should do about it. I looked over their ash analysis data, which indicated a Class F fly ash and should be good for making bricks. But, the water content of the raw material they used (30%) was well too high to form a firm green brick. They are aiming at making 100% fly ash bricks. I suggested them to keep the water content at 12-15% levels and add about 3% of bentonite or searching for a cheaper local clay material as a binder additive.

Time is running quickly; hope for a good year ahead of us.

Best Wishes,
Melissa

-----Original Message-----
From: Tamara Vandivort [mailto:Tamara.Vandivort@mail.wvu.edu]
Sent: Friday, January 06, 2006 7:45 AM
To: Chou, Melissa
Subject: CBRC Quarterly Reports Due Jan. 17

Melissa,

You are so efficient!!! Hope you had a good trip to India. And Happy New Year!

Tammy

CBRC Technical Progress Report
(October 1, 2005 – December 31, 2005)

Project Title: Manufacturing Fired Bricks with Class F Fly Ash from Illinois Basin Coals

Project Number: 02-CBRC-M12 (DOE SIUC 05-13)

Introduction

More than six million tons of Class F fly ash are generated from burning about one hundred million tons of Illinois Basin coal each year. Most of this fly ash has been ponded or landfilled, and is readily available for making fired bricks. Nevertheless, until the brick industry gains more confidence in using fly ash as a raw material for their brick production, evaluation and testing will be needed on a case-by-case basis. The purpose of this project is to determine if the Class F fly ash produced by Cinergy PSI's Cayuga power generation station (CPSIC) is a viable raw material for brick production at Colonial Brick Company (CBC), a brick plant in Indiana near the Illinois border. CBC is located less than five miles from CPSIC, which burns Illinois Basin coals from both Illinois and Indiana.

Task Description

This project has eight tasks.
Task 1: Sample acquisition.
Task 2: Characterization of raw materials, intermediates, and final products.
Task 3: Producing bench-scale commercial-size green bricks and conducting preliminary in-plant firing evaluations.
Task 4: Commercial-scale production. Up to four commercial test runs will be conducted for process optimization.
Task 5: Economic assessment. The critical economic factors in using fly ash as a raw material for brick making will be evaluated.
Task 6: Environmental feasibility study.
Task 7: Public outreach.
Task 8: Quarterly and final reports.

Summary of this Quarter's Accomplishments and Significant Events

Four scale-up production test runs initiated last quarter for making building bricks containing up to 40 vol% (about 37 wt%) fly ash have been completed in this quarter. The strong and attractive bricks were produced with a commercially acceptable yield of greater than 95%. These bricks have far exceeded ASTM building brick specifications and are marketable for the severe weather grade. In addition, PI attended the International Congress on Fly Ash Utilization Conference held in New Delhi, India on December 4 -7, 2005. The scale-up test results for the paving and building bricks were presented via an oral presentation at the conference and through several individual group discussions.

To-Date Accomplishments

The completion of each task in percentage is indicated as follows.

Task 1 - 100%	Task 2 - 80%	Task 3 -100 %	Task 4 - 100%
Task 5 - 80 %	Task 6 - 70%	Task 7 - 100%	Task 8 - 80%

Technical Progress

Technical feasibility evaluation - There were four 2000-building-brick extrusion test runs completed at the CBC in the previous quarter. During this quarter, commercial firing of these extruded bricks has been completed and was followed by CBC's in-plant evaluation and ISGS' engineering evaluation of the fired products. Formulations for each of the four runs are as follows. Run 1 was included as a standard run which used CBC's commercial brick formulation without ash.

Run 1: 0 vol% CiPFA;	85.71 vol% CBCS;	14.29 vol% CBCC
Run 2: 20 vol% CiPFA;	70 vol% CBCS;	10 vol% CBCC
Run 3: 30 vol% CiPFA;	60 vol% CBCS;	10 vol% CBCC
Run 4: 40 vol% CiPFA;	50 vol% CBCS;	10 vol% CBCC

The results from CBC's evaluation indicated that the fired bricks met CBC's own plant specification with respect to physical appearance, color, shrinkage rate and production yield. The four runs successfully produced bricks with a yield of greater than 95%.

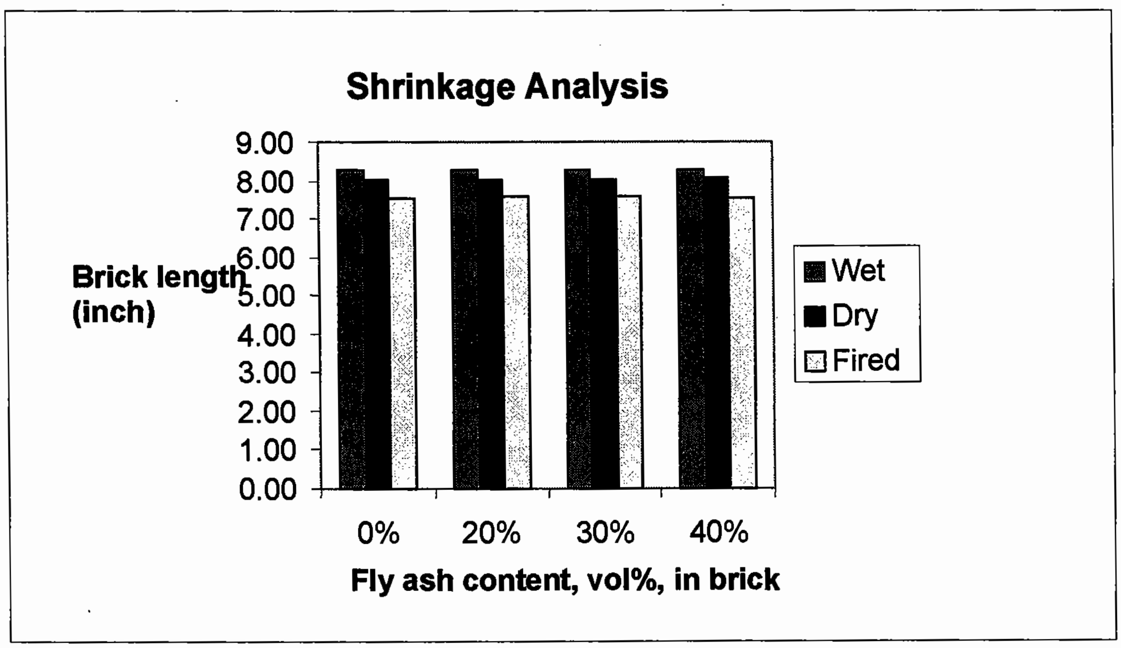


Figure 1: Changes in the brick length after drying and firing

The shrinkage rate was calculated based on the measurement of the brick length. According to CBC, the total (dry plus fired) shrinkage rate must be less than 10% to be commercially acceptable. The length of the fired bricks from each batch shown in Figure 1 was determined by first measuring multiple brick samples selected randomly from the brick pile, then taking an average value from these measurements. The measurements indicated that the total shrinkage rate was between 8 and 9% for each of the four runs.

The ISGS engineering property tests (Table 1) indicated that these bricks far exceed ASTM building brick specifications and are marketable for the severe weather grade. In order to confirm these findings, duplicate tests are currently being conducted on additional brick samples from the scale-up runs.

Table 1: Engineering properties of extruded bricks from scale-up run at CBC

Brick composition, Vol%		CiPFA 0 CBCS 85.71 CBCC 14.29	CiPFA 20 CBCS 70 CBCC 10	CiPFA 30 CBCS 60 CBCC 10	CiPFA 40 CBCS 50 CBCC 10
Max. water absorption	Cold water 24 hr soak,% (< 8wt%)	3.75	4.00	3.93	4.05
	Boiling water 5 hr, %	5.30	6.06	5.89	4.30
	Saturation coefficient	0.71	0.66	0.67	0.94
Fired compressive strength (psi) (Severe weather grade > 8000 psi)		16905	16410	14530	16670
Suction, gm wt gain/minute		5.02	5.62	4.91	2.92

CiPFA: Cinergy Ponded Fly Ash; CBCS: Colonial Brick Company Shale; CBCC: Colonial Brick Company Clay

Economic feasibility evaluation - The economic feasibility of producing fired bricks with fly ash at CBC is an important factor to consider in the commercialization of the process. The process developed for making fired bricks with coal fly ash uses ash to substitute for part of the clay and shale that are typically used in brick making, and has no capital cost involved. This is because the process can be adopted by using conventional machinery. Therefore, the major factors to be considered during economic assessment are the cost of obtaining raw materials and the production costs.

Since fly ash is a byproduct of coal combustion and is readily available throughout the year, and the producer is eager to give it away at little to no cost, the main cost to be considered will be transporting the ash from the power station to the brick plant. A trucking company was contacted to estimate the possible cost of shipping the ash from Cinergy Cayuga plant to CBC. Since the distance between the two locations is less than 5 miles, the shipping company would charge a rate of $65 per hour rather than charging per mile. If the dump truck can carry 25 tons of ash and a maximum time of 2 hours is needed for loading, transporting and unloading of the ash, the overall transportation cost is estimated at $5.20 (= $65 X 2 / 25) per ton.

Using fly ash as a substitute raw material can reduce the annual consumption of clay and shale material and thus reduce the annual mining costs for the brick plant. According to CBC, their annual mining cost is about $143,000 for producing 12 million bricks per year. As mentioned earlier, incorporating fly ash does not incur any initial capital costs because it can be used with existing equipment. Assuming CBC can produce bricks with 40% fly ash at an annual production rate of 12,000,000 bricks per year, the cost of shipping would be $53,040/yr (12,000,000 bricks/yr X 4.25 lb/brick X 1/2000 ton/lb X 5.20 $/ton X 0.4 part ash). The cost savings from mining less material would be $57,200/yr ($143,000 X 0.4 part fly ash). Thus, the difference between $57,200 and $53.040 would create an annual savings of $4160. However, since the power company is saving money because they will not have to place their ash in landfills and holding ponds, they can help with the cost of shipping. If the utility company can pay half of the shipping cost ($2.60 per ton), the brick plant would incur an annual shipping cost of $26,520 (12,000,000 bricks/yr X 4.25 lb/brick X 1/2000 ton/lb X 2.60 $/ton X 0.4 part ash). This shared shipping cost would increase the annual savings for the brick plant to $30,680.

Fly ash is a fine material which does not require additional processing, unlike shale and clay which need crushing and extensive grinding. Therefore, using fly ash as a substitute raw material has an additional benefit of reducing processing costs. CBC is spending $69,000 per year to process their clay and shale for brick making. If fly ash could be used at a rate of 40%, their savings in processing raw material would be $27,600/yr ($69,000 X 0.4). Therefore, when accounting for the shared transportation costs, mining, and processing, the total annual savings for the brick plant producing bricks containing 40 wt% of fly ash would be $58,280.

Plans for Next Period

Analysis (Task 2) will be completed in conjunction with the environmental assessment (Task 6) by analyzing the leachates from various fired brick and raw material formulations to determine the concentration of different metal ions that are leachable under extreme acid-rain conditions. The economic feasibility evaluation (Task 5) will be finalized according to the up-to-date quotes for the transportation estimates. In addition, the market for fired bricks will be updated. A final report will be prepared (Task 8) for the CBRC. Dr. Y. Paul Chugh plans to conduct a site visit at ISGS for the project.

Expenditures Above $500

The cost for PI's travel to attend and present project results to the International Congress on Ash Utilization Conference was $2771.36.

Western Regional Projects
Active Projects

02-CBRC-W9 - O'Neill

Power Plant Combustion By-Products for Improved Crop Productivity of Agricultural Soils

02-CBRC-W9

Michael O' Neil

TECHNICAL PROGRESS REPORT

Power Plant Combustion Byproducts for Improved Crop Productivity of Agricultural Soils

New Mexico State University, Agricultural Science Center at Farmington
Mick O'Neill (PI)

Reporting period ending January 15, 2006

ACRONYM LIST

CCBs	Coal Combustion Byproducts – specifically referring to fly ash, bottom ash, and scrubber slurry obtained from Four Corners Power Plant, Farmington, New Mexico.
EC	Electrical Conductivity
NAPI	Navajo Agricultural Products Industry
NMSU ASC	New Mexico State University Agricultural Science Center at Farmington
NMSU Agro/Hort	New Mexico State University Department of Agronomy and Horticulture, Las Cruces, New Mexico
SAR	Sodium Adsorption Ratio
SWAT Lab	Soil, Water, and Air Testing Lab, NMSU, Las Cruces, NM

INTRODUCTION

Two coal combustion power plants in the Four Corners region consume approximately 14.5 million metric tons of sub-bituminous coal on an annual basis for the generation of electricity. In addition to electricity, these power plants also generate substantial coal combustion byproducts (CCBs) in the form of 3.4 million metric tons of ash and 0.39 million metric tons of flue gas desulfurization (FGD) materials. Near the two power plants is the Navajo Agricultural Products Industry (NAPI), a large commercial farm currently operating nearly 600 automatic center pivot irrigation systems on 25,000 ha of farmland. Soil texture on the NAPI farm is generally sandy to sandy loam with limited water-holding capacity, low inherent nutrient status, and elevated pH. The addition of bottom ash, fly ash, and/or FGD materials to agricultural soils may increase water-holding capacity and contribute to the soil pool of micronutrients available for plant uptake.

This project is designed to 1) identify potentially beneficial and harmful constituents of CCBs; 2) characterize the water-holding capacity of CCB-amended soils; and 3) to demonstrate potential increased productivity of these soils with the addition of

CCBs from local coal combustion power plants. This study is a collaborative project with New Mexico State University, the Navajo Agricultural Products Industry, and the Arizona Public Service (APS) Four Corners Power Plant. The demonstration of environmentally sound management strategies for applying CCBs to agricultural lands would address regional and national priorities established by the U.S. Department of Energy National Energy Technology Laboratory and the Combustion Byproducts Recycling Consortium for the increased utilization of these products.

TASK DESCRIPTION JULY 15 – OCTOBER 14, 2005 REPORTING PERIOD

The following is a list of tasks and accomplishments outlined below initiated or completed during this reporting period.

#	TASK	STATUS	Institution/Location
1.	Recruit a graduate student into the NMSU Department of Agronomy and Horticulture soil science program	Completed	NMSU Agro/Hort
2.	Obtain start-up funds/lab inspection and quality assurance compliance	Completed	NMSU Agro/Hort
3.	Characterize CCBs obtained from Four Corners Power plant, Farmington for agriculturally significant macro and micro-nutrient content.	Completed	NAPI Lab
4.	Establish Hybrid Poplar pilot container of study utilizing CCBs as soil amendment at application rates of 10 and 20 tons/acre.	Completed	NMSU ASC
5.	Establish Hybrid Poplar container greenhouse trial utilizing CCBs as soil amendment at application rates of 10 and 20 tons/acre.	1. Study terminated 2. Lab analysis ongoing	NMSU Agro/Hort and NAPI Lab
6.	Establish second Hybrid Poplar greenhouse trial utilizing fly ash.	1. Study terminated 2. Lab analysis ongoing	NMSU Agro/Hort and NAPI Lab
7.	Establish Sorghum container greenhouse trial utilizing CCBs as soil amendment at application rates of 10 and 20 tons/acre.	1. Study terminated 2. Lab analysis ongoing	NMSU Agro/Hort and NAPI Lab

#	TASK	STATUS	Institution/Location
8.	Establish Column leachate study utilizing CCBs. Methodology established to simulate field conditions at the NMSU ASC with soil amended with CCBs at 10 and 20 ton/acre application rates.	1.Study terminated 2.Lab analysis ongoing	NMSU Agro/Hort and SWAT Lab
9.	Establish moisture release curves with soil amended with CCBs at 10 and 20 ton/acre application rates.	Not Started	NMSU Agro/Hort

SUMMARY OF THIS QUARTER'S ACCOMPLISHMENTS & SIGNIFICANT EVENTS

Activities reported in the 3rd Quarter have been largely carried into this reporting period. The activities to date have included continued processing of soil samples for salinity, pH, sodium adsorption ratio and plant available essential elements and trace metals. Stem material from two hybrid poplar container studies have been processed for acid digestion according to the Eden 1A method for trace metal analysis by ICP. Soil samples were removed in segments from the Soil Column Study and were acid digested according to EPA Method 3051A for subsequent metal analysis. Data that has been generated is being compiled for statistical analysis.

TECHNICAL PROGRESS

The greenhouse studies have been completed. In Task 5, a Doak sandy loam soil from Farmington was amended with either fly ash, bottom ash or scrubber slurry (APS Four Corners Power Plant) at two rates: 10 and 20 T/ acre. Task 6 consisted of hybrid poplar cultivated in the greenhouse in soil amended with fly ash only at two rates common for land applied manures: 10 and 20 T/acre. A third treatment based on DTPA plant available iron (Fe) contained within the fly ash was applied at an equivalent rate of 32.8 T/acre according to soil test results. A commercially available chelated Fe (Sprint 138) was applied at a labeled rate to respective containers as a fertilizer check, and control containers received no amending. Preliminary data from Task 6 showed increased leaf areas and leaf dry weights from the Fly Ash 20T/acre treatment (Figure 1 and 2) indicating potential positive benefits to biomass accumulation.

Processing of plant material for chemical analysis in task 5 and 6 is complete. Processing entailed grinding leaf and stem samples to a fine powder for dry ashing in a muffle furnace at the NAPI lab (Farmington) or microwave assisted acid digestion in closed Teflon vessels according to Eden 1A (Miller, 1998) and USEPA 3051A (USEPA, 1998) methods at the Soils Research Group lab (Las Cruces). A majority of the processed soil, leaf, and stem material from Tasks 5 and 6 has been or is currently being analyzed for plant available essential elements and potential trace metal accumulation (Ag, As, Ba, Cd, Cr, Pb,) on the NAPI Lab ICP. Concurrent to this, soil from Task 6 is being analyzed for salinity (EC), sodium adsorption ratio (SAR), and pH at the NMSU Soil Group Lab, Las Cruces (Figure 3). The SAR analysis for Task 6 will be conducted on the SWAT Lab ICP, Las Cruces.

The Leachate column study (Task 8) of 27 columns filled with a Doak sandy loam soil amended with the various CCBs was terminated in mid August. Soil from the 30 cm long columns was removed in September by dissecting each column in 2.5 cm sections for a total of 12 samples per column representing an experimental 0-30 cm soil profile depth. Soil samples were air dried and acid digested according to the above mentioned USEPA method 3051A at Las Cruces. These samples were then taken to Farmington in mid-December and are currently being analyzed on the NAPI lab ICP for trace metal content to determine the adsorption or movement of any potentially hazardous element within the soil profile.

ADDITIONAL WORK PLANS FOR JANUARY 15-APRIL 14, 2005 REPORTING PERIOD

Chemical analysis for Tasks 5-8 has taken longer than expected because of method and instrumentation experimentation and coordination of activities between two distant locations (Las Cruces and Farmington). It is anticipated that all chemical analysis should be completed by the end of the reporting period. Data will be analyzed in SAS to determine any significant differences in chemical content versus the controls. Results of these studies are now pending the completion of chemical analysis currently ongoing at both the NAPI lab and NMSU Soils group lab or the compellation of data generated up to this point from both locations.

The recent hiring of a Soil Physicist by the NMSU Soil Research Group will aid in the assessment of soil physical parameters, specifically, moisture release curves (Task 9) which will be initiated as soon as the chemical analysis portion of the studies are complete. The moisture release curves will establish water holding capacity of soil amended with agricultural rates of the various CCBs. These data will be combined with soil and biomass data generated from the greenhouse studies to begin to establish agricultural utilization significance of CCBs in the Four Corners region.

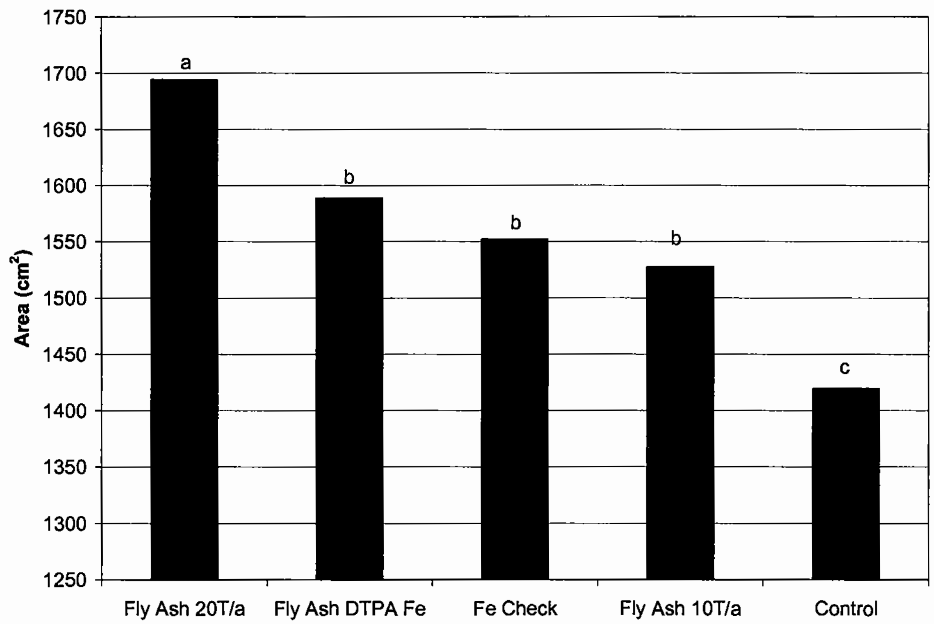


Figure 1. Mean leaf areas harvested from Task 6 Greenhouse Study (bars with different letters are significant at the $p<.0001$; LSD = 104.849).

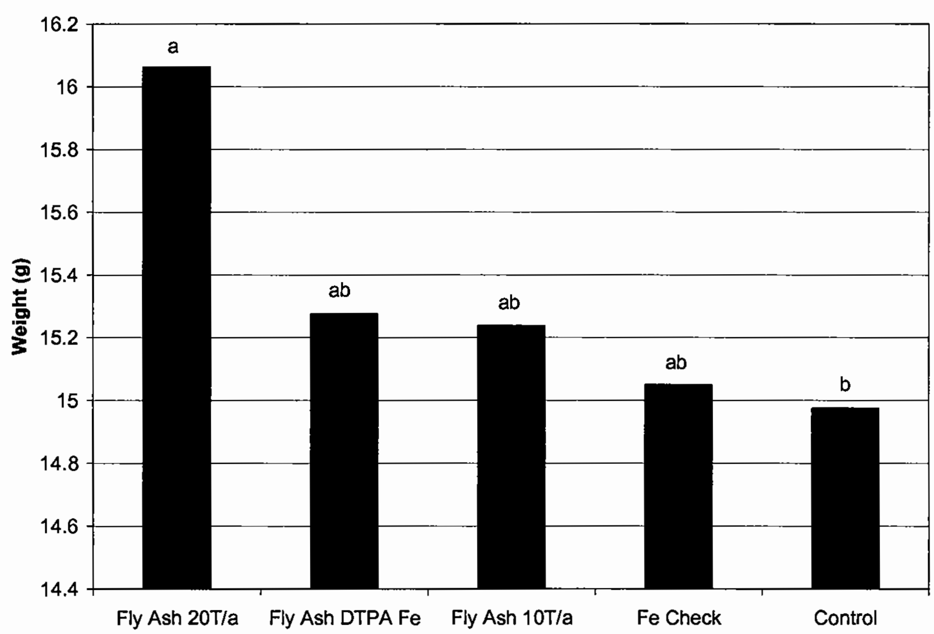


Figure 2. Mean leaf dry weights harvested from Task 6 Greenhouse Study (bars with different letters are significant at the $p<.0001$; LSD = 1.03).

Figure 3. Preparation of saturated paste extracts for EC and SAR analysis of Task 6

REFERENCES

Miller, R.O. 1998. Microwave digestion of plant tissue in a closed vessel, p. 69-73, In Y. P. Karla, ed. Handbook of Reference Methods for Plant Analysis. CRC Press, New York.

USEPA. 1998. Microwave assisted acid digestion of sediments, sludges, soils, and oils Method 3051A. US Environmental Protection Agency, Washington, D.C.

Appendix A

Fall 2005 Issue of Ashlines

Volume 6, Number 3 Fall 2005

COMBUSTION BYPRODUCTS RECYCLING CONSORTIUM

Ashlines

a program of the National Mine Land Reclamation Center at West Virginia University, in cooperation with the U.S. Department of Energy-National Energy Technology Laboratory
www.netl.doe.gov

To promote and support the commercially viable and environmentally sound recycling of coal combustion byproducts for productive uses, through scientific research, development, and field testing

Forging Ahead with CCB Research: Can Fly Ash Replace Sand in Foundry Operations?

Robert Purgert, P.I.

Foundries in the United States use about 100 million tons of sand per year in their operations, which is roughly the same amount of coal combustion byproducts (CCBs) produced annually. Since natural sand has some disadvantages for use in the foundry industry and CCBs are potential substitutes for sand, interchangeability, plus supply-and-demand would seem to be suggesting that foundries research the benefits of CCBs over natural sand.

The introduction of fly ash and bottom ash into the foundry industry could create a new use for CCBs and perhaps solve some of the problems associated with the use of natural sand, the traditional base material of foundry molding and core mixtures.

Natural sand has three major drawbacks in foundry use:

Pouring gray iron into sand molds with cores made of fly ash.

1. Because grains of natural sand, like any granular material, are nonhomogeneous in size and shape, they have different dust contents.
2. Natural sand must be excavated, cleaned, and segregated before use.
3. Natural sand poses a potential health risk for workers and is being scrutinized as a potential

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Forging Ahead with CCB Research: Can Fly Ash Replace Sand in Foundry Operations?
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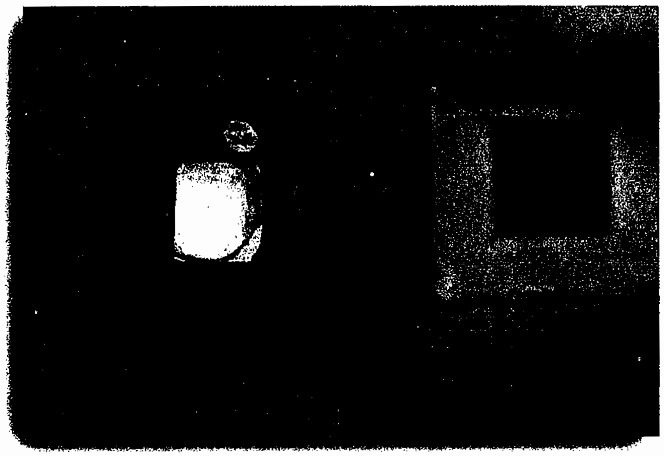

Cores with blue and pink coatings nested in dry sand molds prior to pour.

cause of silicosis in workers exposed to crystalline silica (quartz), which is common in foundry sands.

Under a program funded by the Combustion Byproducts Recycling Consortium (CBRC), the Energy Industries of Ohio has just completed a project designed to demonstrate the suitability of fly ash as a replacement for traditional foundry sands. This study elaborates on the findings of an earlier CBRC project (#00-CBRC-E42).

Project costs were shared by a project team that included the General Motors Company (GM) casting plant in Defiance, Ohio; Oak Ridge National Laboratory; Edison Materials Technology Center; Foundry Research Institute of Krakow, Poland; Kent State University; FirstEnergy Corporation; and the Dayton Power & Light Company.

The study explored the feasibility of substituting CCBs for foundry sands, specifically, by replacing fly ash for the virgin silica sand typically used in the foundry molds and cores employed by the automotive industry.

Background

During the earlier CBRC project, researchers determined that CCBs could be used in a number of applications as substitutes for traditional foundry sands in the production of metal castings. Foundry sands are used to make molds and cores that approximate the shapes of the metal product or cast. Molten metal is poured into the mold to form a cast metal part or component. The mold defines the outside areas of the casting, and the core shapes the interior passageways and openings.

Previous studies established that CCBs were suitable as a replacements for foundry sands in both mold and core applications. Molds made from CCBs were successfully used under laboratory conditions to make castings of both ferrous and nonferrous alloys. A significant finding was the ability to substitute 100% ash for traditional foundry sand in the chemically bonded (or dry sand) types of applications that are often used for making cores.

The outcomes of the initial project highlighted a need for further study to refine production techniques and formulas for the ash and binder systems. Another important activity identified for the next phase was to ensure that actual production techniques could be used with little modification.

Objectives

The recently completed project was undertaken to demonstrate the use of fly ash in applications similar to those used for actual production. Automotive industry iron castings were chosen as a subject because of their widespread use and the quantity of sand used each year in their production. Automotive castings also have stringent quality require-

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Forging Ahead with CCB Research: Can Fly Ash Replace Sand in Foundry Operations?

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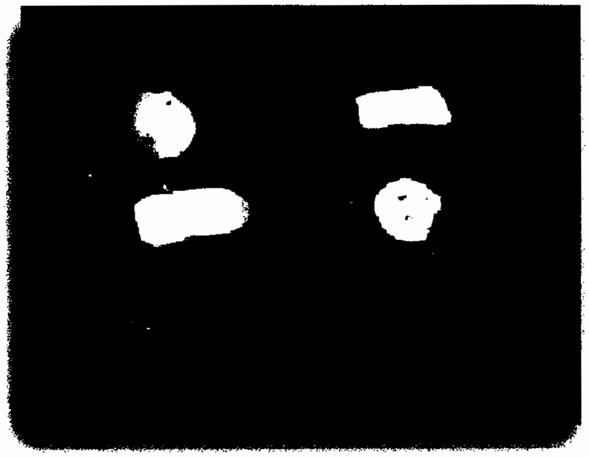

Iron castings in sand molds with fly ash cores.

ments , which makes them a good test subject for determining the production readiness of the fly ash molds and cores.

Selection of Ash Mixtures and Binding Systems

Fly ash from the FirstEnergy Eastlake Plant in the United States and, for comparison, from the Skawina Power Plant located near the Foundry Research Institute of Krakow, Poland, were used in the study.

To contrast the ash with that used in the earlier phase of the project, detailed investigations of its chemical composition; phase constitution; density distribution; and individual fractions, toxicity, and thermal characteristics were conducted.

A binding system was then chosen to ensure that the cores and molds closely approximated those being used in the production process at the General Motors casting plant in Defiance, Ohio. In an effort to match the high degree of permeability of the GM cores and molds, a binding system of organic and inorganic binders was determined to be the most suitable.

The technological properties of various fly ash mold and core mixtures were tested, and the three most promising chemical compositions and fabrication methods were then employed in a number of trials on the casting of gray and ductile irons.

Casting Trials

The trials took place at the Energy Industries of Ohio Casting Center, a full-scale working foundry. Cores made of fly ash were used in sand molds to make iron castings. Both the molds and cores closely approximated those used in the actual production process at GM.

Macroscopic examinations of the castings to check the surface conditions and gas content revealed that the permeability coupled with the high-calcium content of the ash caused considerable out-gassing, which affected the surface quality of the castings. This was directly attributed to the high calcium content of the ash used in this study compared with that of the ash used in the first analysis.

Final trials took place in the late summer of 2005. Sample cores were prepared for testing, and a visit to the GM casting plant was made to review the test plan and observe the actual process. During this visit, it was noted that a coating was applied to the sand cores prior to use in the casting molds. The coating was needed to achieve the desired smooth surface finish and to reduce permeability of the core. This detail is significant for two reasons:

1. Fly ash has a relatively very fine grain size when made into cores. This creates a very fine

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Forging Ahead with CCB Research: Can Fly Ash Replace Sand in Foundry Operations?

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surface finish, which may make it unnecessary for GM to coat the cores in the future.

2. When the ash is mixed with a single binder system, the permeability is reduced significantly; again, possibly negating the need for the coating. Initially in this study the intent had been to increase permeability to match the GM cores as closely as possible.

Subsequent trials demonstrated that fly ash cores could be produced with the traditional inorganic binder system and coated with the types of coatings currently used by GM.

Tests and a demonstration for GM officials were conducted, during which the cores did indeed hold up to the process, but considerable out-gassing was again noted. This time the gasses were released in a concentrated jet, probably at the point of the weakest area of the coating shell.

Conclusions

After analyzing the differences between these findings and those of the earlier study, it was concluded that the type of fly ash plays a significant role in determining its suitability for use in casting applications. The fly ash used in the initial study was from Dayton Power & Light and was wet collected. The ash used for this series of tests was from FirstEnergy's Eastlake plant and was dry collected.

From this attempt to create production-type casting materials, it was concluded that certain types of fly ash offer the ability to replace foundry sand systems for making cores and molds, even in applications for high-temperature castings such as iron. However, the following technical obstacles first must be addressed prior to commercialization:

- To reduce out-gassing, the ash must contain a low level of calcium.
- The ash should be of a size distribution that would not require changes to screens and vents used in current sand systems.
- A binder system that will permit ease of knock-out after casting must be defined. The cores made from 100% fly ash required a greater amount of binder than traditional sands, resulting in a high binder volume, which made it more difficult to remove the castings.

In addition to defining the suitability of certain ashes for metal casting, this project revealed that ashes and binder systems can impact a wide array of engineering characteristics in the cores, including the level of permeability. Another significant finding was that the surface finish of castings made with fly ash cores has certain advantages that may eliminate the need for applying expensive coatings to the cores and then waiting for them to dry prior to casting.

This project highlights the need for further study of fly ash as a substitute for foundry sand and demonstrates several potential advantages of employing ash in the metal casting industry. A subsequent project is planned for identifying the optimal binding systems and binder volumes for fly ash cores.

For more information about this project (#02-CBRC-E10), or to view the final report, please visit the CBRC web site at http://wvwri.nrcce.wvu.edu/programs/cbrc/ or contact the CBRC at cbrc@wvu.edu.

> ***"The introduction of fly ash and bottom ash into the foundry industry could create a new use for CCBs and perhaps overcome some of the disadvantages of natural sand, the traditional base material of foundry molding and core mixtures."***

Calendar

February 23, 2006
Ramada Inn
Marquette, MI

Workshop on Recycling Opportunities for Fly Ash and Other Coal Combustion Products in Concrete and Construction Materials

The purpose of this workshop is to bring participants up to date on the latest information about recycling applications for coal combustion products in concrete and other construction materials. Presentations will give important information on technical, environmental, and economic advantages of using coal ash in ordinary, everyday construction applications. The workshop will be of interest to the construction industry, concrete producers and manufactures, contractors, and to utilities and other industries producing coal combustion by-products, as well as architects, engineers and academic researchers.

Workshop registration fee of $35 ($45, if registering after February 17) includes handouts, refreshments, and lunch. Complete information about the conference, including agenda and speaker information, at: www.cbu.uwm.edu. Call 414/229-4105 or email tarun@uwm.edu.

Sponsored by UWM Center for By-Products Utilization; We Energies; Mineral Resources Technologies, a Cemex Company; and co-sponsored by Michigan Technological Institute and Wisconsin Public Service Corporation.

Calls for Papers

Sustainable Construction Materials and Technologies

Coventry University, Coventry, UK
Monday June 11–Wednesday, June 13, 2007
www.uwm.edu/dept/cbu/coventry.html

Abstracts of 200-300 words to be submitted by email to by March 2006 to p.claisse@coventry.ac.uk.

This conference will highlight case studies and applied research that shows new and innovative ways of achieving sustainability of construction materials and technologies. Papers are invited on all the different materials used in construction, including cementitious materials (fly ash, wood ash, silica fume, slag, natural pozzolans, and others); aggregates; admixtures, concrete; timber; masonry; metals; plastics; glass; bitumen; lime; and gypsum. Papers on paints, adhesives, preservatives, and preservation processes are also welcome.

23rd Annual International Pittsburgh Coal Conference

Pittsburgh, PA
Monday, Sept. 25–Thursday, September 28, 2006
www.engr.pitt.edu/pcc

Papers may be contributed in all subject areas dealing with coal technologies and related policy issues. Submit a one-page abstract by email on or before March 1, 2006 to pcc@engr.pitt.edu

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National Steering Committee Meets to Select Pre-Proposals

The National Steering Committee met September 16, 2005 in Pittsburgh, PA to select pre-proposals from which to invite applicants to submit full proposals. Of the 52 pre-proposals received, 19 applicants were invited to submit full proposals by December 15, 2005. The Steering Committee will meet in early 2006 to select which full proposals should be recommended to the U.S. Department of Energy-National Energy Technology Laboratory for funding.

Ashlines is published quarterly by the Combustion Byproducts Recycling Consortium, headquarted at West Virginia University in Morgantown, WV. Would you like to be on the CBRC electronic mailing list? If so, please send an email to cbrc@nrcce.wvu.edu.

Volume 6, Number 3 Fall 2005

COMBUSTION BYPRODUCTS RECYCLING CONSORTIUM

Ashlines

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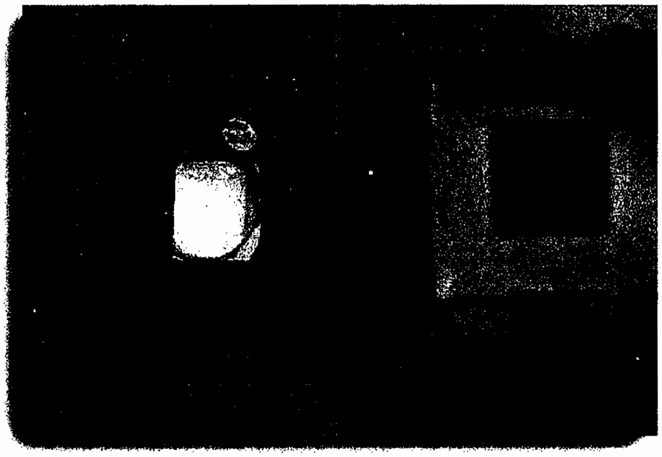

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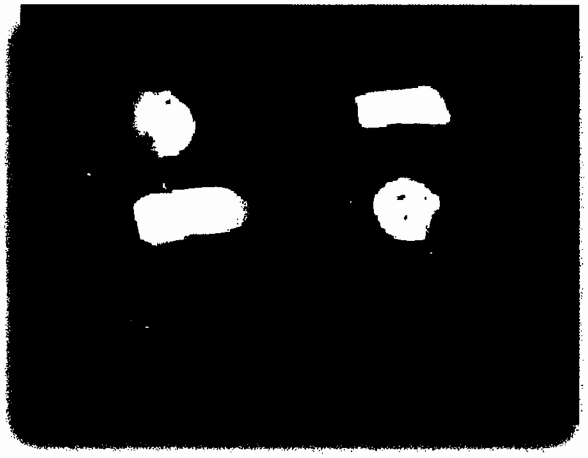

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A binding system was then chosen to ensure that the cores and molds closely approximated those being used in the production process at the General Motors casting plant in Defiance, Ohio. In an effort to match the high degree of permeability of the GM cores and molds, a binding system of organic and inorganic binders was determined to be the most suitable.

The technological properties of various fly ash mold and core mixtures were tested, and the three most promising chemical compositions and fabrication methods were then employed in a number of trials on the casting of gray and ductile irons.

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The trials took place at the Energy Industries of Ohio Casting Center, a full-scale working foundry. Cores made of fly ash were used in sand molds to make iron castings. Both the molds and cores closely approximated those used in the actual production process at GM.

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Tests and a demonstration for GM officials were conducted, during which the cores did indeed hold up to the process, but considerable out-gassing was again noted. This time the gasses were released in a concentrated jet, probably at the point of the weakest area of the coating shell.

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From this attempt to create production-type casting materials, it was concluded that certain types of fly ash offer the ability to replace foundry sand systems for making cores and molds, even in applications for high-temperature castings such as iron. However, the following technical obstacles first must be addressed prior to commercialization:

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This project highlights the need for further study of fly ash as a substitute for foundry sand and demonstrates several potential advantages of employing ash in the metal casting industry. A subsequent project is planned for identifying the optimal binding systems and binder volumes for fly ash cores.

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Sponsored by UWM Center for By-Products Utilization; We Energies; Mineral Resources Technologies, a Cemex Company; and co-sponsored by Michigan Technological Institute and Wisconsin Public Service Corporation.

Calls for Papers

Sustainable Construction Materials and Technologies

Coventry University, Coventry, UK
Monday June 11–Wednesday, June 13, 2007
www.uwm.edu/dept/cbu/coventry.html

Abstracts of 200-300 words to be submitted by email to by March 2006 to p.claisse@coventry.ac.uk.

This conference will highlight case studies and applied research that shows new and innovative ways of achieving sustainability of construction materials and technologies. Papers are invited on all the different materials used in construction, including cementitious materials (fly ash, wood ash, silica fume, slag, natural pozzolans, and others); aggregates; admixtures, concrete; timber; masonry; metals; plastics; glass; bitumen; lime; and gypsum. Papers on paints, adhesives, preservatives, and preservation processes are also welcome.

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COMBUSTION BYPRODUCTS RECYCLING CONSORTIUM

Ashlines

a program of the National Mine Land Reclamation Center at West Virginia University, in cooperation with the U.S. Department of Energy-National Energy Technology Laboratory www.netl.doe.gov

To promote and support the commercially viable and environmentally sound recycling of coal combustion byproducts for productive uses, through scientific research, development, and field testing

Forging Ahead with CCB Research: Can Fly Ash Replace Sand in Foundry Operations?

Robert Purgert, P.I.

Foundries in the United States use about 100 million tons of sand per year in their operations, which is roughly the same amount of coal combustion byproducts (CCBs) produced annually. Since natural sand has some disadvantages for use in the foundry industry and CCBs are potential substitutes for sand, interchangeability, plus supply-and-demand would seem to be suggesting that foundries research the benefits of CCBs over natural sand.

The introduction of fly ash and bottom ash into the foundry industry could create a new use for CCBs and perhaps solve some of the problems associated with the use of natural sand, the traditional base material of foundry molding and core mixtures.

Natural sand has three major drawbacks in foundry use:

Pouring gray iron into sand molds with cores made of fly ash.

1. Because grains of natural sand, like any granular material, are nonhomogeneous in size and shape, they have different dust contents.
2. Natural sand must be excavated, cleaned, and segregated before use.
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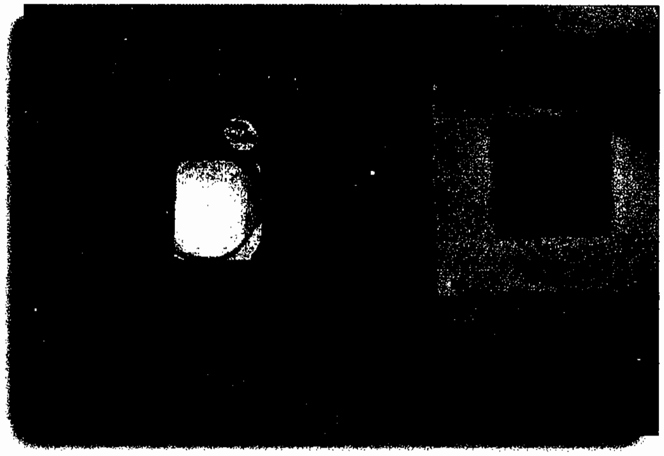

Cores with blue and pink coatings nested in dry sand molds prior to pour.

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Under a program funded by the Combustion Byproducts Recycling Consortium (CBRC), the Energy Industries of Ohio has just completed a project designed to demonstrate the suitability of fly ash as a replacement for traditional foundry sands. This study elaborates on the findings of an earlier CBRC project (#00-CBRC-E42).

Project costs were shared by a project team that included the General Motors Company (GM) casting plant in Defiance, Ohio; Oak Ridge National Laboratory; Edison Materials Technology Center; Foundry Research Institute of Krakow, Poland; Kent State University; FirstEnergy Corporation; and the Dayton Power & Light Company.

The study explored the feasibility of substituting CCBs for foundry sands, specifically, by replacing fly ash for the virgin silica sand typically used in the foundry molds and cores employed by the automotive industry.

Background

During the earlier CBRC project, researchers determined that CCBs could be used in a number of applications as substitutes for traditional foundry sands in the production of metal castings. Foundry sands are used to make molds and cores that approximate the shapes of the metal product or cast. Molten metal is poured into the mold to form a cast metal part or component. The mold defines the outside areas of the casting, and the core shapes the interior passageways and openings.

Previous studies established that CCBs were suitable as a replacements for foundry sands in both mold and core applications. Molds made from CCBs were successfully used under laboratory conditions to make castings of both ferrous and nonferrous alloys. A significant finding was the ability to substitute 100% ash for traditional foundry sand in the chemically bonded (or dry sand) types of applications that are often used for making cores.

The outcomes of the initial project highlighted a need for further study to refine production techniques and formulas for the ash and binder systems. Another important activity identified for the next phase was to ensure that actual production techniques could be used with little modification.

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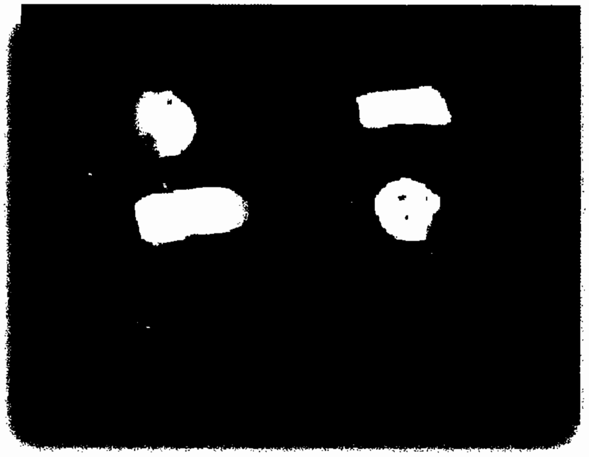

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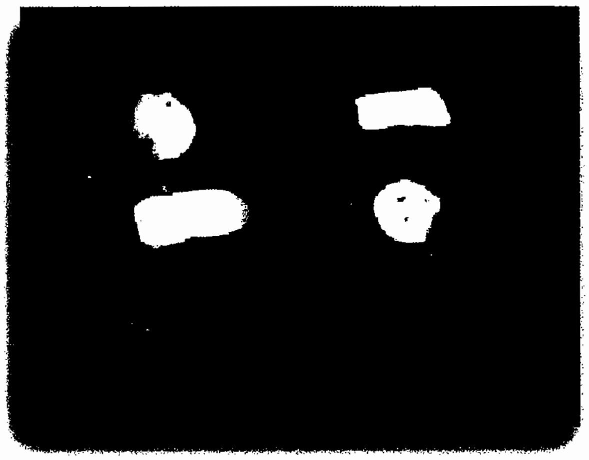

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In addition to defining the suitability of certain ashes for metal casting, this project revealed that ashes and binder systems can impact a wide array of engineering characteristics in the cores, including the level of permeability. Another significant finding was that the surface finish of castings made with fly ash cores has certain advantages that may eliminate the need for applying expensive coatings to the cores and then waiting for them to dry prior to casting.

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Sponsored by UWM Center for By-Products Utilization; We Energies; Mineral Resources Technologies, a Cemex Company; and co-sponsored by Michigan Technological Institute and Wisconsin Public Service Corporation.

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COMBUSTION BYPRODUCTS RECYCLING CONSORTIUM

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a program of the National Mine Land Reclamation Center at West Virginia University, in cooperation with the U.S. Department of Energy-National Energy Technology Laboratory www.netl.doe.gov

To promote and support the commercially viable and environmentally sound recycling of coal combustion byproducts for productive uses, through scientific research, development, and field testing

Forging Ahead with CCB Research: Can Fly Ash Replace Sand in Foundry Operations?

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Foundries in the United States use about 100 million tons of sand per year in their operations, which is roughly the same amount of coal combustion byproducts (CCBs) produced annually. Since natural sand has some disadvantages for use in the foundry industry and CCBs are potential substitutes for sand, interchangeability, plus supply-and-demand would seem to be suggesting that foundries research the benefits of CCBs over natural sand.

The introduction of fly ash and bottom ash into the foundry industry could create a new use for CCBs and perhaps solve some of the problems associated with the use of natural sand, the traditional base material of foundry molding and core mixtures.

Natural sand has three major drawbacks in foundry use:

Pouring gray iron into sand molds with cores made of fly ash.

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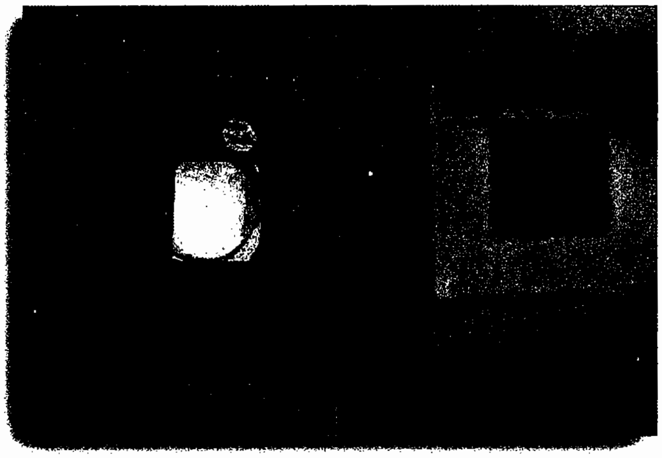

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Project costs were shared by a project team that included the General Motors Company (GM) casting plant in Defiance, Ohio; Oak Ridge National Laboratory; Edison Materials Technology Center; Foundry Research Institute of Krakow, Poland; Kent State University; FirstEnergy Corporation; and the Dayton Power & Light Company.

The study explored the feasibility of substituting CCBs for foundry sands, specifically, by replacing fly ash for the virgin silica sand typically used in the foundry molds and cores employed by the automotive industry.

Background

During the earlier CBRC project, researchers determined that CCBs could be used in a number of applications as substitutes for traditional foundry sands in the production of metal castings. Foundry sands are used to make molds and cores that approximate the shapes of the metal product or cast. Molten metal is poured into the mold to form a cast metal part or component. The mold defines the outside areas of the casting, and the core shapes the interior passageways and openings.

Previous studies established that CCBs were suitable as a replacements for foundry sands in both mold and core applications. Molds made from CCBs were successfully used under laboratory conditions to make castings of both ferrous and nonferrous alloys. A significant finding was the ability to substitute 100% ash for traditional foundry sand in the chemically bonded (or dry sand) types of applications that are often used for making cores.

The outcomes of the initial project highlighted a need for further study to refine production techniques and formulas for the ash and binder systems. Another important activity identified for the next phase was to ensure that actual production techniques could be used with little modification.

Objectives

The recently completed project was undertaken to demonstrate the use of fly ash in applications similar to those used for actual production. Automotive industry iron castings were chosen as a subject because of their widespread use and the quantity of sand used each year in their production. Automotive castings also have stringent quality require-

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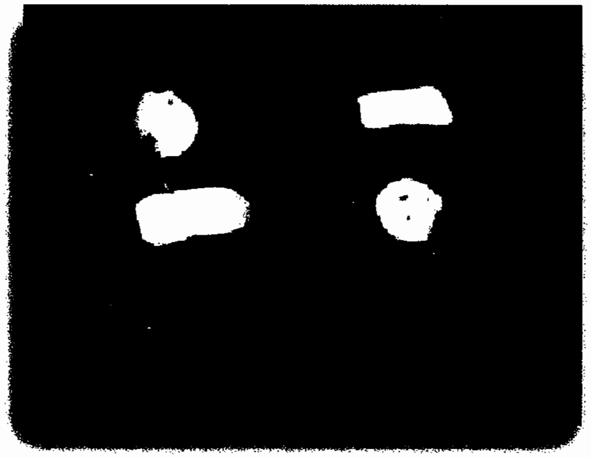

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To contrast the ash with that used in the earlier phase of the project, detailed investigations of its chemical composition; phase constitution; density distribution; and individual fractions, toxicity, and thermal characteristics were conducted.

A binding system was then chosen to ensure that the cores and molds closely approximated those being used in the production process at the General Motors casting plant in Defiance, Ohio. In an effort to match the high degree of permeability of the GM cores and molds, a binding system of organic and inorganic binders was determined to be the most suitable.

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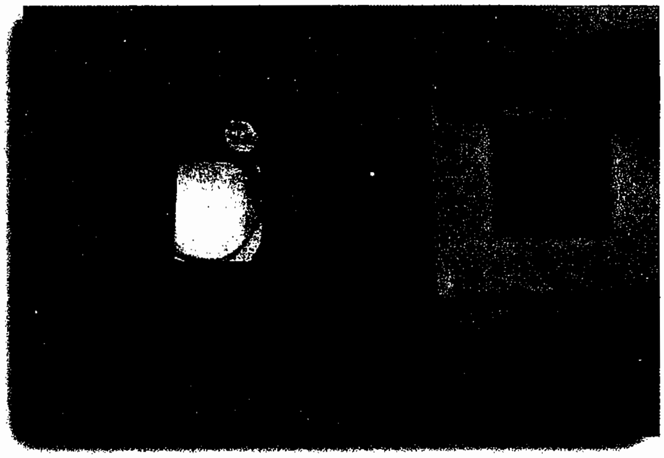

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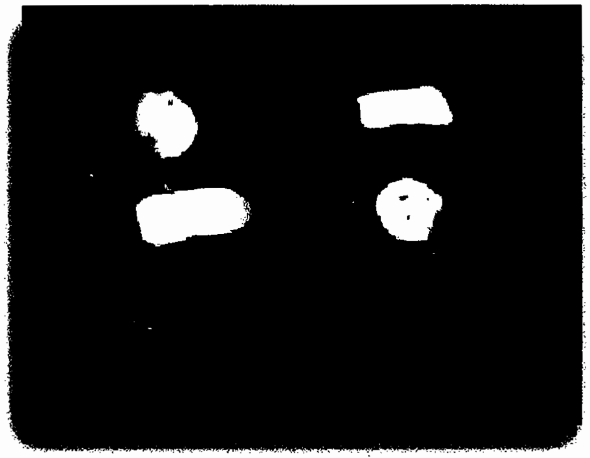

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Tests and a demonstration for GM officials were conducted, during which the cores did indeed hold up to the process, but considerable out-gassing was again noted. This time the gasses were released in a concentrated jet, probably at the point of the weakest area of the coating shell.

Conclusions

After analyzing the differences between these findings and those of the earlier study, it was concluded that the type of fly ash plays a significant role in determining its suitability for use in casting applications. The fly ash used in the initial study was from Dayton Power & Light and was wet collected. The ash used for this series of tests was from FirstEnergy's Eastlake plant and was dry collected.

From this attempt to create production-type casting materials, it was concluded that certain types of fly ash offer the ability to replace foundry sand systems for making cores and molds, even in applications for high-temperature castings such as iron. However, the following technical obstacles first must be addressed prior to commercialization:

- To reduce out-gassing, the ash must contain a low level of calcium.
- The ash should be of a size distribution that would not require changes to screens and vents used in current sand systems.
- A binder system that will permit ease of knock-out after casting must be defined. The cores made from 100% fly ash required a greater amount of binder than traditional sands, resulting in a high binder volume, which made it more difficult to remove the castings.

"The introduction of fly ash and bottom ash into the foundry industry could create a new use for CCBs and perhaps overcome some of the disadvantages of natural sand, the traditional base material of foundry molding and core mixtures."

In addition to defining the suitability of certain ashes for metal casting, this project revealed that ashes and binder systems can impact a wide array of engineering characteristics in the cores, including the level of permeability. Another significant finding was that the surface finish of castings made with fly ash cores has certain advantages that may eliminate the need for applying expensive coatings to the cores and then waiting for them to dry prior to casting.

This project highlights the need for further study of fly ash as a substitute for foundry sand and demonstrates several potential advantages of employing ash in the metal casting industry. A subsequent project is planned for identifying the optimal binding systems and binder volumes for fly ash cores.

For more information about this project (#02-CBRC-E10), or to view the final report, please visit the CBRC web site at http://wvwri.nrcce.wvu.edu/programs/cbrc/ or contact the CBRC at cbrc@wvu.edu.

Calendar

February 23, 2006
Ramada Inn
Marquette, MI

Workshop on Recycling Opportunities for Fly Ash and Other Coal Combustion Products in Concrete and Construction Materials

The purpose of this workshop is to bring participants up to date on the latest information about recycling applications for coal combustion products in concrete and other construction materials. Presentations will give important information on technical, environmental, and economic advantages of using coal ash in ordinary, everyday construction applications. The workshop will be of interest to the construction industry, concrete producers and manufactures, contractors, and to utilities and other industries producing coal combustion by-products, as well as architects, engineers and academic researchers.

Workshop registration fee of $35 ($45, if registering after February 17) includes handouts, refreshments, and lunch. Complete information about the conference, including agenda and speaker information, at: www.cbu.uwm.edu. Call 414/229-4105 or email tarun@uwm.edu.

Sponsored by UWM Center for By-Products Utilization; We Energies; Mineral Resources Technologies, a Cemex Company; and co-sponsored by Michigan Technological Institute and Wisconsin Public Service Corporation.

Calls for Papers

Sustainable Construction Materials and Technologies

Coventry University, Coventry, UK
Monday June 11–Wednesday, June 13, 2007
www.uwm.edu/dept/cbu/coventry.html

Abstracts of 200-300 words to be submitted by email to by March 2006 to p.claisse@coventry.ac.uk.

This conference will highlight case studies and applied research that shows new and innovative ways of achieving sustainability of construction materials and technologies. Papers are invited on all the different materials used in construction, including cementitious materials (fly ash, wood ash, silica fume, slag, natural pozzolans, and others); aggregates; admixtures, concrete; timber; masonry; metals; plastics; glass; bitumen; lime; and gypsum. Papers on paints, adhesives, preservatives, and preservation processes are also welcome.

23rd Annual International Pittsburgh Coal Conference

Pittsburgh, PA
Monday, Sept. 25–Thursday, September 28, 2006
www.engr.pitt.edu/pcc

Papers may be contributed in all subject areas dealing with coal technologies and related policy issues. Submit a one-page abstract by email on or before March 1, 2006 to pcc@engr.pitt.edu

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National Steering Committee Meets to Select Pre-Proposals

The National Steering Committee met September 16, 2005 in Pittsburgh, PA to select pre-proposals from which to invite applicants to submit full proposals. Of the 52 pre-proposals received, 19 applicants were invited to submit full proposals by December 15, 2005. The Steering Committee will meet in early 2006 to select which full proposals should be recommended to the U.S. Department of Energy-National Energy Technology Laboratory for funding.

Combustion Byproducts Recycling Consortium

Ashlines is published quarterly by the Combustion Byproducts Recycling Consortium, headquarted at West Virginia University in Morgantown, WV. Would you like to be on the CBRC electronic mailing list? If so, please send an email to cbrc@nrcce.wvu.edu.

Appendix B

Final Report
02-CBRC-E10

Commercialization of Production Foundry Molds made from CCB's for High Volume Automotive Applications

Robert M. Purgert, PI

NETL F 510.1-5#
(12/1999) OPI=PS10
(Previous Editions Obsolete)

REQUEST FOR PATENT CLEARANCE FOR RELEASE OF CONTRACTED RESEARCH DOCUMENTS

◆Contract Agreement No.
DE-FC26-98FT40028

Name & Phone No. of DOE COR
William Aljoe
(412)-386-6569

TO: ☐ For Technical Reports
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U.S. Department of Energy - NETL
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Argonne, IL 60439
FAX: (630) 252-2779

A. CONTRACTOR ACTION (CONTRACTOR COMPLETES PART A. 1-5)

1. Document Title: Commercialization Demonstration For Production Foundry Molds Made From CCB'S FOR HIGH VOLUME AUTOMOTIVE APPLICATIONS

2. Type of Document: ☐ Technical Progress Report ☐ Topical Report ☒ Final Technical Report
☐ Abstract ☐ Technical Paper ☐ Journal Article ☐ Conference Presentation
☐ Other (please specify): ______

3. Date clearance needed: ______

◆4. Patent information.

Yes	No	
☐	☒	Is any patentable subject matter disclosed in the report?
☐ N/A	☐	If so, has an invention disclosure been submitted to DOE Patent Counsel? If yes, identify disclosure number or DOE Case Number ______
☐	☒	Are there any patent-related objections to the release of this report? If so, state the objections.

◆5. Signed Edward J. Galaska, Secretary-Treasurer (Contractor) Date 11-2-05
Edward J. Galaska
Name & Phone No. Energy Industries of Ohio Tel. 216-643-2952
Address Park Center One, Suite 200, 6100 Oak Tree Boulevard, Independence, OH 44131

B. DOE PATENT COUNSEL ACTION

☐ Patent clearance for release of the above-identified document is granted.
☐ Other: ______

Signed ______ Date ______

(Patent Attorney)

◆ Must be completed by the contractor.

COMMERCIALIZTION DEMONSTRATION FOR PRODUCTION FOUNDRY MOLDS MADE FROM CCB'S FOR HIGH VOLUME AUTOMOTIVE APPLICATIONS

Energy Industries Of Ohio

Type of Report:	**Final Report**
Reporting Period Start:	**October 2004**
Reporting Period End:	**October 2005**
Principal Authors	**Professor Jerzy Sobczak** **Mr. Robert Purgert**
Co-Authors:	**Andrzej Balinski, D.Sc.,** **Pawel Darlak, M.Sc.**
Issue Date:	**November 2005**
DOE Award Number:	**98-166-EIO**
Name of Submitting Organization:	**Energy Industries of Ohio** **6100 Oak Tree Boulevard** **Suite 200** **Independence, OH 44131**

Disclaimer

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Abstract

The study performed and outlined in this Final Report discusses the results of experiments and trials concerning the application of fly ash as a base material substitution for foundry sands (FASAND mixture) to produce iron castings for the automotive industry. Two types of fly ashes were examined: the fly ash from the FirstEnergy Eastlake Plant (USA) and, for comparison, the fly ash from the Skawina Power Plant located near the Foundry Research Institute of Krakow, Poland (a strategic partner of the Energy Industries of Ohio) from where the visiting professor working on the project is the Deputy Director. The ash selection was based on promising results obtained in an earlier study which warranted "live fire" type testing undertaken in this program approximating actual commercial conditions to the fullest extent possible.

The fly ashes underwent detailed investigation regarding their chemical composition, phase constitution, density distribution of individual fractions, toxicity, and thermal characteristics. After initial selection of a binding system, the technological properties of the FASAND type mixtures were tested. Using the three most promising chemical compositions and fabrication methods, under the local conditions at Energy Industries of Ohio Casting Development Center and Foundry Research Institute a number of trials were conducted on casting of gray and ductile irons, using cores that approximated those utilized in the actual production of castings provided to the project team by the General Motors Defiance, Ohio casting plant.

The experimental cores were made to approximate the sample cores provided by General Motors by employing a combination organic/inorganic binder system. This process was developed to insure that the cores closely approximated those being used in the production process at the General Motors facility. The experimental cores were then used in a number of casting tests.

The trial castings were subjected to macroscopic examinations to check the surface condition and gas content. Final trials were to take place during early summer 2005. Sample cores were prepared for testing and a final walk thru of the process and site visit to General Motors was undertaken. It was at this time that it was learned GM is currently using a coating mixture on the cores due to the permeability and other factors. This was somewhat of a re-direction as the effort was attempting to introduce permeability into the cores given the samples that were provided and the general property of very limited permeability that is afforded when using a fly ash medium.

Testing continued however to determine the suitability of the fly ash received from FirstEnergy's Eastlake plant. Unfortunately, the results were less than hoped for mainly due to the differences in the fly ash being used on the current project having a higher calcium and possibly carbon content vs. those used on the previous project. It was learned that the Eastlake plant had switched to a blended coal which altered these characteristics of the ash. The findings are important, however, from the standpoint of defining the envelope of which ashes are the most suitable candidates for foundry sand replacement applications.

A subsequent trial was conducted employing the coating material on the cores made with traditional inorganic binder systems to minimize permeability and determine whether the out-gassing could also be reduced by avoiding an organic binder system. Tests using both types of core coating materials were conducted and in this case the noticeable out-gassing continued but appeared to be more "focused" as the gases were released in a concentrated jet, probably at the point of the weakest area of the coating shell. However, the surface finish of the cores were of high interest to GM due to the smooth, tightly packed appearance and feel.

The conclusions from this study are that certain fly ash materials offer the ability to replace the current sand systems for making cores if the following technical hurdles are addressed:

1. *Determining the maximum levels of calcium and unburned carbon permissible in FASAND (ash with low levels of these contaminants have been found to be very suitable).*
2. *The small particle size fly ashes can be used with the present core-making processes by altering the "venting" or by finding mixtures of ash and sand that will negate any costly changes to the process or equipment.*
3. *A binder system that will meet the casting, molding and knock-out requirements of the automotive industry to insure ease of removal after casting.*

The conclusion is that the project was successful for defining ashes that are and are not suitable for metal casting, that ashes and binder systems are capable of producing a wide array of engineered characteristics in the cores to include level of permeability; and that the surface finish of fly ash produced castings have certain advantages which may negate the need for expensive coatings being applied to the cores and the consequent cure times needed for drying prior to casting.

Contents

Introduction

1. Executive Summary

Industrial wastes and by-products are often undesired materials formed during the processing of raw materials for industrial or other useful endeavors such as power generation. Many, if not properly handled, may be harmful and/or strenuous to the environment. These industrial by-product materials which include oils, slag, ashes, mineral products and metals, are, however, much more homogeneous than the composition of municipal waste thus making them strong candidates for beneficial re-use in other applications.

One such material "produced" by the power generation industry is fly ash. Fly ash materials are a by-product resulting from the combustion of coal at thermal power plants. Fly ash could present serious ecological problems if not properly stored or disposed of which increases the ultimate costs passed on to the industrial and residential consumer. Therefore, the development of suitable scientific, technical and economic solutions for fly ash utilization are very pressing, and even more timely given the current energy situation facing the United States. The U.S. acquires more than half of its electricity needs (52%) from coal based power generation generating approximately 70 million tons of fly ash annually.

Potential uses of fly ash waste materials have been sought throughout the world with many novel and useful approaches being found. One area that offers significant opportunity is the use of fly ash as a replacement for foundry sand in mold and core production (FASANDS) [8, 9].

The traditional base material of foundry molding and core mixtures is natural sand in different mineralogical and chemical variations, characterized by different surface morphologies, and of differing physical properties. All these parameters affect, to a great degree, the technological properties of the ready foundry mixture. Granular materials of any type, being a natural product, have a very serious disadvantageous feature in common - that is - the grains are non-homogeneous in size and shape, and have different contents of dust fraction (dimensions < 0.02 mm). The use of natural sand as a base material in foundry mixtures also entails the necessity of excavating it from a natural deposit, with further cleaning and segregation needed prior to being used. And, finally, the use of natural sand is being scrutinized very closely as being a cause of silicosis in workers exposed to quartz type sands over extend periods giving further impetus to studying alternative molding mediums such as fly ash for use as a substitute.

Depending on the type of the sand and binder used to hold the sand in the desired shape to form a mold or core, one of the most important parameters of foundry sands, is the thermal conductivity (λ) which assumes the values from about 1.5 W/m·K - for silica sand-based mixtures, up to about 3.0 W/m·K for zircon sand-based mixtures. These high values of the coefficient λ in the case of sand-based foundry mixtures may be the reason for numerous casting defects related to rapid heat transfer from the cast metal and difficulties in effective control of the directional solidification process [4].

The better insulation properties of foundry sands substituted by fly ash was expected to have a consequent reduction in the number of and severity of casting defects caused by the restrained metal's shrinkage. The preliminary investigation and trials conducted thus far indicate that fly ash may not only offer this advantage but offer a much more environment-friendly process as well as a cost-effective alternative solution to defects when compared to the presently used foundry sands. Some testing was accomplished during the investigation stages that indicates a low heat conductivity of fly ash, which - depending on morphological fractions - is from 0.01 W/m·K, to 0.3 W/m·K.

In a previous study, work was done by the Energy Industries of Ohio in conjunction with the Foundry Research Institute in an attempt to visualize the effect of fly ash (DP&L, First Energy and LEG) as an additive to green sand and as a filler for chemically bonded sand [8]. The physical properties such as dimensions (screen distribution), density, characteristic temperatures and chemical properties (pH value) as well as technological parameters (compression strength, tensile strength, permeability, friability and compatibility) for wide range of FASANDS were investigated.

It was concluded during that earlier study that the fly ash could be utilized as a replacement and filler in foundry sands used for molds and core production, however that some fly ash was more suitable than others particularly in ferrous applications due to the high pouring temperature. However, almost all types of ash were suitable for molds and core making for many non ferrous metals such as, Cu-, Al- and Zn-based alloys.

The current project presented a new set of challenges when attempting to prepare the ash for ultimate use in an iron production foundry. It was found that ash containing higher levels of calcium were considerably problematic when considering the amount of out-gassing experienced. However, the current project did also confirm the progressive interest by the automotive industry to pursue working with the suitable fly ash due to its fine surface finish and the possibility of eliminating a coating process currently employed on the production cores.

The previous study confirmed the possibility of using 100% DP&L fly ash as a sand substitute for the production of chemically bonded molds and cores. That project led to the attempt under the current program to "move" the knowledge into the production environment and determine whether other types of ash were similarly suitable candidates. The current project established that fly ash containing higher calcium contents and possibly traces of unburned coal or carbon are unsuitable for this application but did further define the limits or envelope parameters of the ash suitable for this application. Further work employing ash that only has characteristics such as a higher melting point, lower calcium, etc. will be attempted in the future through ongoing efforts.

Besides the above mentioned, measurable, economic effects resulting from the use of fly ash as a base material of foundry sands, some recognition regarding the non-quantifiable effects obtained should also be noted:

- *ecological aspect* – the utilization of fly ash reduces the impact upon the environment by achieving a lower solid waste stream currently being landfilled.
- *economic and social aspects* – fly ash can be a very attractive secondary raw material, considering its low price and practically unlimited availability. Its rational use can bring some quantifiable financial profits to those who produce this waste (capital-saving investments, access to special funds for environmental protection, reduced fees for storage of waste, etc.) and to potential employees through new job creation. The utilization of fly ash may also benefit specific coal mines, since, any future large-scale utilization of this waste material will require long-term agreements made between the thermal power plants and specific mines for gathering coal from specific deposits to ensure the required consistency of the fly ash supply.
- *research - technical aspect* – research of other beneficial uses of fly ash spurred by the creation of a new unique market application should lead to the creation of other new potential opportunities in various sectors of economy.

As natural resource raw materials become more costly with ever higher global demand caused by developing nations undergoing economic expansion, the incentive to explore and locate low cost, environmentally beneficial alternative uses of production by-products becomes an ever more near term goal.[2,3,5,6,7] The use of properly processed, valuable waste materials such as fly ash as a base aggregate of foundry sands will achieve this goal while also preserving natural resources. These attributes, coupled with the wide-scale savings connected with exploration and processing of minerals while minimizing the need to transform large areas of the natural landscape for mining or landfilling offer significant beneficial opportunities.

EXPERIMENTAL

2. Experimental General information

The following materials were utilized for investigations of fly ash materials for foundry sand (FASAND) cores:

1. **Fly ash** from the following Power Plants: FirstEnergy's Eastlake Plant (EP), Cleveland, Ohio; and, for comparison, from Skawina (Skawina), Poland.
2. **Water glass** (sodium silicate) of modulus M = 2,1, density at 20^0C ρ = 1,520 g/cm^3 and an absolute viscosity of 50,0 cP, modified chemically with organofunctional, morphoactive additives, hardened thermally and chemically by ethylene glycol diacetate.
3. **Hydrolyzed ethyl silicate** „40", hardened with aqueous solution of ammonium hydroxide NH_4OH of 5% concentration
4. **Diacitate of ethylene glycol (ester)** without any modification by glycol propylene, with a density of 1.12 g/cm^2 and acid number of 16 mg KOH/g.
5. **Portland cement** with chemical compound: $3CaO{\cdot}SiO_2$ – 55%, $2CaO{\cdot}SiO_2$ – 20%, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ – 10%, $3CaO{\cdot}Al_2O_3$ – 10%, $Ca(SO_4){\cdot}2H_2O$ – 5%
6. **Acid sodium carbonate** $NaHCO_3$ with density at 20^0C ρ = 2,22 g/cm^3 and mole weight = 84.01 g/mole
7. Composition of **various chemical compounds** trade name Genifor GK-B
8. **Silica sand** with main fraction 0.20/0.32/0.16 and homogeneity index 88
9. **Molochite** with fractions from 0 to 0.125 mm and chemical compound: SiO_2 – 54,56%, Al_2O_3 – 42,55%, K_2O – 1.75%, Fe_2O_3 – 0.75%, TiO_2 – 0.08%, MgO, 0.1%, CaO – 0.1%, Na_2O – 0.1%

For pouring gray iron (before and after spheroidization for nodular iron) the following chemical compositions (wt.%) were utilized:

C = 3.5	Si = 2.52	Mn = 0.25
P = 0.1	S = 0.002	Ni = 0.18
Mo = 0.06	Cu = 0.2	Fe = rest

RESULTS AND DISCUSSIONS

3. Investigation of fly ash in respect to chemical composition, mineralogy, density distribution, thermal and radiological behavior

The investigation was carried out on two types of fly ash: on the fly ash from the Cleveland, Ohio Eastlake Plant, supplied by FirstEnergy and designated as „EP", and additionally, for the sake of comparison, fly ash from Skawina Power Plant, designated as „Skawina".

The purpose of the investigation was to examine some of the selected physio-chemical properties of the fly ash to determine its chemistry and gas composition and to evaluate the level of toxicity. This was done to permit a comparison to that ash used in the previous proof of concept program. The following examinations were made:

-chemical composition
-phase constitution
-density distribution
-thermal behavior
-toxicity
-natural radioactivity (including concentration of natural nuclides)

<u>Chemical composition</u>

Fly ash is formed during coal combustion from the internal and external mineral matter present in the coal. These minerals are compounds such as alumino-silicates, sulfides, and carbonates.

The quantity and quality (the chemical and mineralogical composition) of fly ash formed during the coal combustion process depends on the type of coal (brown coal, hard coal, etc.), on the type of furnace (pulverized-fuel fired furnace, fluidized-bed grate furnace, etc.), and on the type of combustion process (e.g. low-emission burners, desulfurizing by dry and/or semi-dry methods).

To better illustrate the expected chemical composition and phase constitution of fly ash, the table below gives examples of products formed as a result of the thermal transformation of some minerals during the process of coal combustion.

Table 3.1 Schematic description of the thermal transformation of minerals during coal combustion

Group of minerals	Transformation temperature [°C]	Product of thermal transformation
Quartz	870	transformed into tridymite
Aluminosilicates (feldspar)	1150 - 1200	melts down with liberation of volatile alkalies
Argillaceous aluminosilicates	450 – 550	undergoes dehydroxylation
Kaolinite	800	transformed into sillimanite, which in the presence of fluxes (e.g. iron) is further transformed into mullite
or	1000 – 1100	mullite is formed

Muskovite	400 – 800 1000 – 1100	undergoes two-stage dehydroxylation mullite is formed
Montmorillonite	150 – 250 700 1000 – 1150	undergoes dehydratation undergoes dehydroxylation mullite is formed
Carbonates: Siderite	450 – 500	decomposed into FeO and CO_2 and transformed into magnetite
Dolomite	765 – 895	decomposes
Calcite	900	decomposes and the formed CaO reacts with SO_2
Iron sulfides	500 – 510	decomposed into hematite Fe_2O_3 and SO_2
Zinc and lead sulfides	about 500 < about 1000	decompose oxides of these metals are transformed into volatile matters
Iron hydroxides	110 – 150	lose water and are transformed into hematite
Aluminium hydroxides	600	lose water of crystallization

The content (in % by weight) of the main and trace elements (calculated in terms of oxides) was determined in the examined fly ashes by atomic absorption spectroscopy and atomic emission spectroscopy induced by a plasma jet (argon) on ICP MS ELAM 6100 and ICP AES Plasma apparatus.

Table 3.2 Percent content of selected elements in the examined fly ashes

Oxides content in fly ash	EP	Skawina
SiO_2	64.98	81.66
Al_2O_3	10.93	6.690
Fe_2O_3	6.965	4.374
CaO	12.41	4.293
MgO	1.950	1.577
Na_2O	0.531	0.211
K_2O	0.3464	0.4015
ZnO	0.0186	0.0103
CrO_3	0.0145	0.0115
CdO	0.0002	3.214E-05
PbO	0.0081	0.0081
As_2O_5	0.0048	0.0010
SO_3	1.593	0.279

Generally speaking, the fly ash from Skawina has the chemical composition typical of fly ashes produced during the combustion of hard coal in a pulverized-fuel fired furnace; the Eastlake Plant fly ash, contrary to what was expected at the beginning of the project due to a blending of coals, is also fly ash originating from the hard coal combustion process conducted in a pulverized-fuel fired furnace, except that the sulfur compounds are most probably removed from this fly ash during combustion by a FSI technique (adding $CaCO_3$ to the furnace).

Phase constitution

The phase constitution of the fly ashes and their derivatives was determined by an X-ray diffraction technique on a PHILIPS APD X-Pert PW3020 apparatus under CuKα radiation monochromatized with reflexive graphite monochromator.

Similar to the results of the chemical analysis, the predominant phase constituents are, besides an amorphous phase, quartz and mullite as the chief constituents, and hematite and derivatives of aluminosilicate - illite (Fig.3.1). An X-ray diffraction pattern of the Eastlake Plant fly ash reveals the presence of anhydrite, which confirms the presumed presence in this fly ash of the products for a desulfurizing treatment (hence weak reflexes from anhydrite) (Fig.3.2).

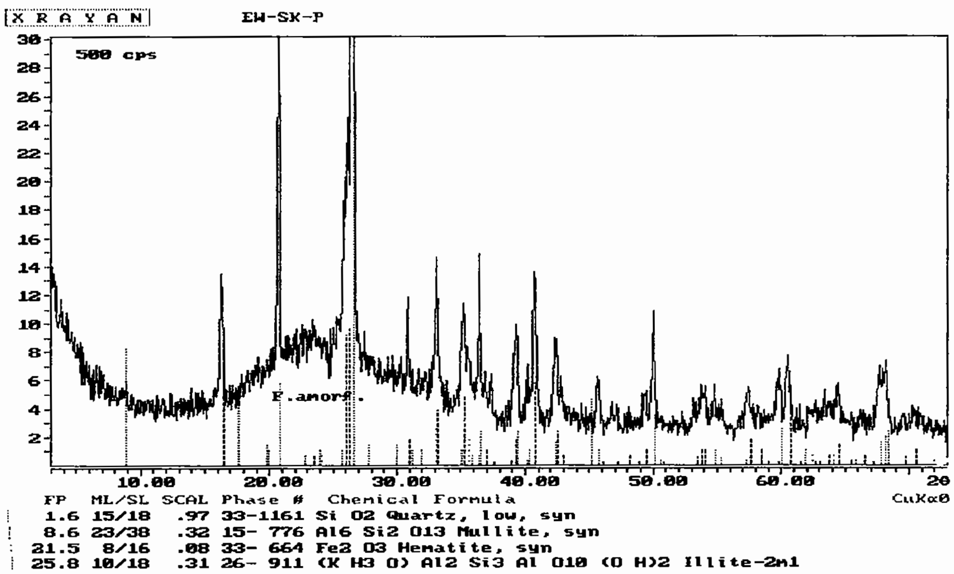


Fig.3.1. X-ray diffraction pattern of the Skawina fly ash

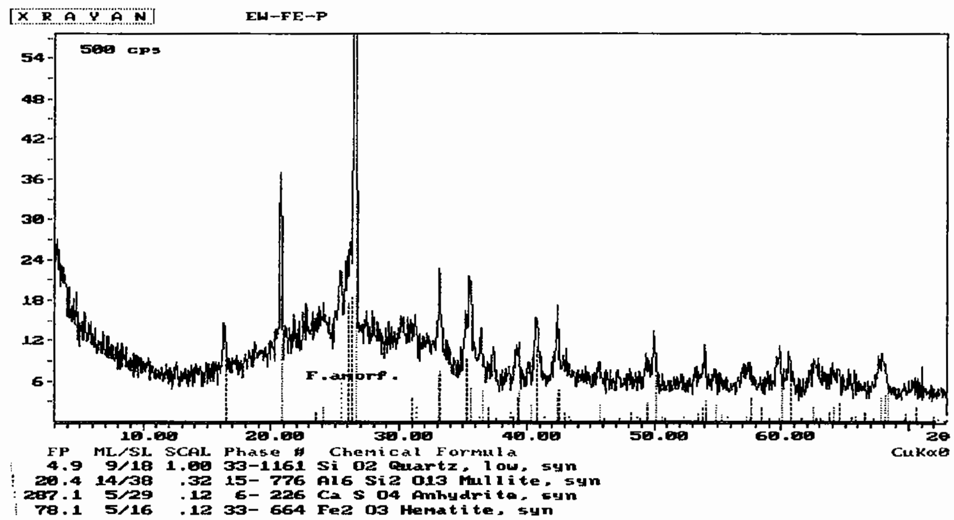


Fig.3.2. X-ray diffraction pattern of the Eastlake Plant fly ash

After holding at 800°C for 14h, the phase constitution of the fly ash remained practically unchanged (Fig.3.3). Along with the same phases as observed previously (slightly more distinct reflex from hematite at theta 35.75), some weak reflexes from albite started appearing. The change of color in the fly ash from Skawina after the thermal treatment is related to the removal of some unburned matter that occurred during this treatment.

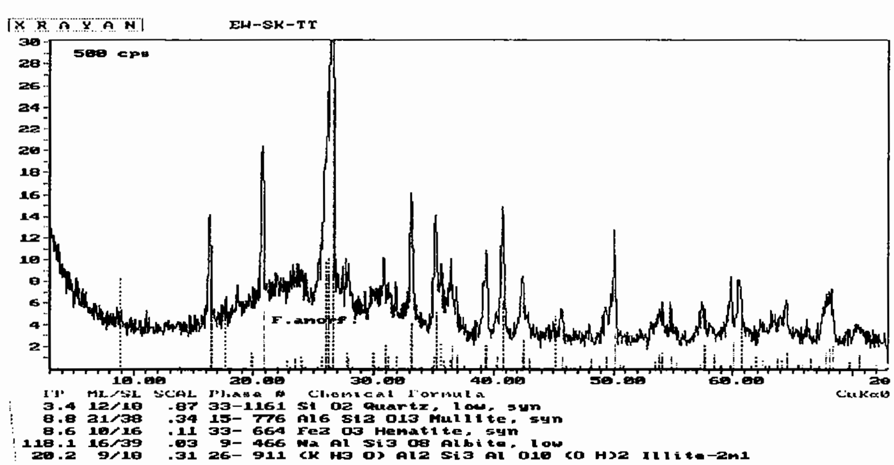


Fig.3.3. X-ray diffraction pattern of the Skawina fly ash after thermal treatment at 800°C for 14h

Density distribution

To determine the density distribution of various fractions present in the fly ash produced at the Eastlake Plant, some experiments were made using liquids characterized by a density 3 times higher than the density of water but with relatively low viscosity. From various trade/commercial products available on the market and used for the purpose of segregation, *sodium polytungstate – SPT* was selected for our trial. This selection was due to its density being able to reach the value of about 3 g/cm^3 with stable and low viscosity well preserved at room temperature (Fig.3.4)

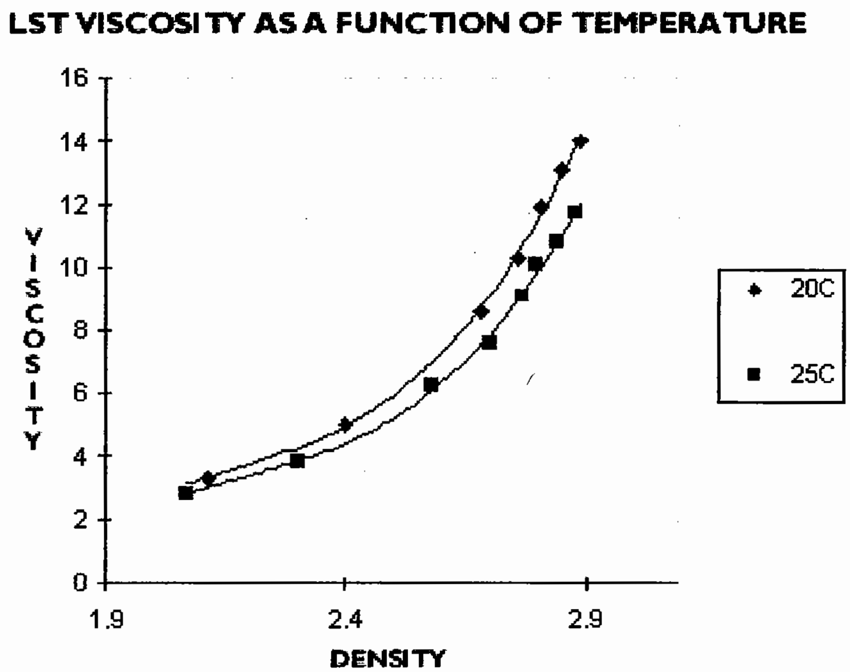


Fig.3.4. Changes in viscosity of heavy liquid (SPT) vs. density and temperature

The trials to separate the fly ash particles in a gravitational field by applying the resultant forces of displacement in a column of liquid failed to give satisfactory results. The reason was probably due to the very small difference between the density of the liquid and that of dust fractions, as well the effect of the viscosity and particles wetting by the liquid due to the phenomena of flotation and sedimentation. Therefore it was necessary to design a simple system which would allow or obtain a higher acceleration (Fig.3.5) and higher force of displacement needed for an effective separation of fractions.

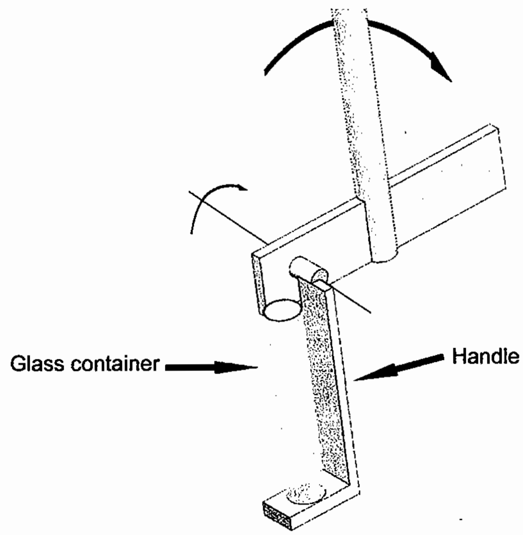


Fig.3.5. Schematic representation of a set for separation of fractions present in fly ash

Raising the value of acceleration to a level higher than the acceleration of gravity, i.e. g = 9.81 m/s^2, is possible by effectively utilizing the phenomenon of centripetal acceleration during a circular motion. The design of a centrifugal device assumed that the acceleration should reach the value 20 times higher than the acceleration of gravity and, to ensure safe operation of the device, its rotational speed should not exceed 2,000 rpm.

Applying the equation of centripetal acceleration during uniform circular motion:

$$a_{centr} = \omega^2 \cdot R \ ;$$

where:

a_{centr} – the centripetal acceleration,
ω – the angular velocity,
R – the radius of rotation,

it was calculated that the arm of the device should have the length of about 20 cm. Within these operating parameters the time for separation of the individual fractions should be, depending on the density of the applied liquid, no more than 5 minutes maximum.

The density distribution of the individual fractions was divided into four groups, starting with a maximum density of the liquid amounting to 3 g/cm^3 (0.108 lb/in^3) reducing this to the next value in steps of 0.5 g/cm^2 (0.018 lb/in^3) until the moment when all fractions present in the fly ash were examined. The percent content of a given fraction was estimated by measuring the length of the visible fields containing fly ash (Fig.3.6) and making the next respective calculations using the following equation:

$$\lambda = \frac{a}{a + | b} \cdot 100\%$$

where:

λ – the percent content of a fraction,

a, b – the length of the visible fly ash - containing field

As a result of the conducted experiments, the percent content of fractions characterized by various densities was calculated. Basing on the obtained data it can be clearly stated that in the examined fly ash the main components are particles with the density comprised in the range of 3 – 2.5 g/cm^2, (0.108 lb/in^3 - 0.090 lb/in^3) which is very valuable information if the fly ash is to be utilized as a reinforcing phase of aluminum composites (Fig.3.7).

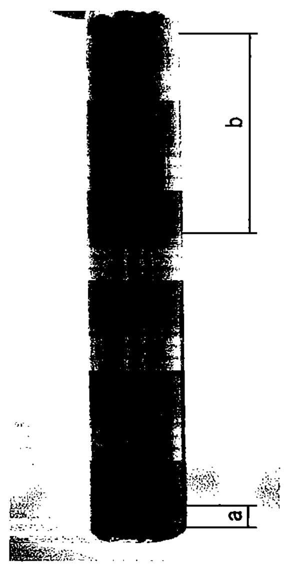


Fig.3.6. Appearance of sample after centrifugal separation of fly ash fractions

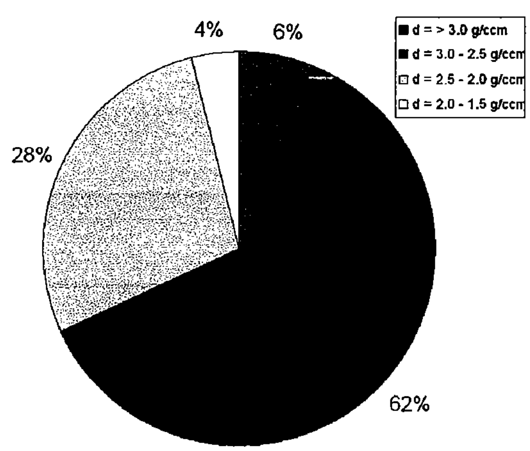


Fig.3.7. Percent content of fly ash fractions vs. density

Characteristic temperatures

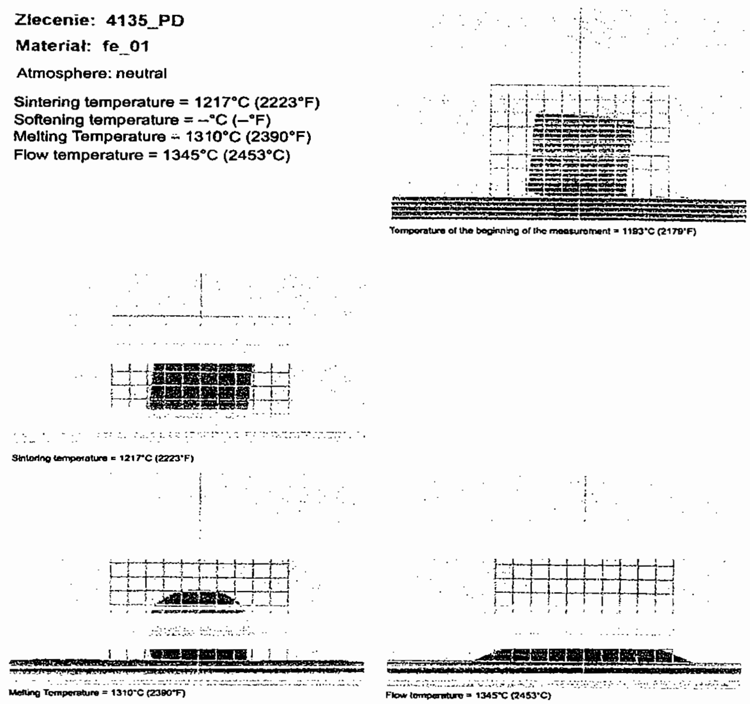
The characteristic temperatures for fly ashes regarding their respective temperatures for sintering, softening, melting and flow were estimated by heating fly ash cylindrical samples in the air using a high temperature microscope PR-$^{25}/_{1750}$ (Figs.3.8 – 3.9). For each material, three samples were tested to determine the changes in sample height (red line); wideness (blue line); its shape factor (green line) and flatness of the sample tip (khaki line). For comparison, the melting point of quartz sand was also measured and shown for comparison purposes. The results of investigations are shown in the following Tables.

Foundry Research Institute
Zakład Technologii
30-418 KRAKOW
ul. Zakopiańska 73
tel. (48)(12) 261-85-42, fax 66-54-78
Pomiar wykonano na urządzeniu PR-25/1750

Indeks: ir41AQ01

Zlecenie: 4135_PD
Materiał: fe_01
Atmosphere: neutral

Sintering temperature = 1217°C (2223°F)
Softening temperature = –°C (–°F)
Melting Temperature = 1310°C (2390°F)
Flow temperature = 1345°C (2453°C)



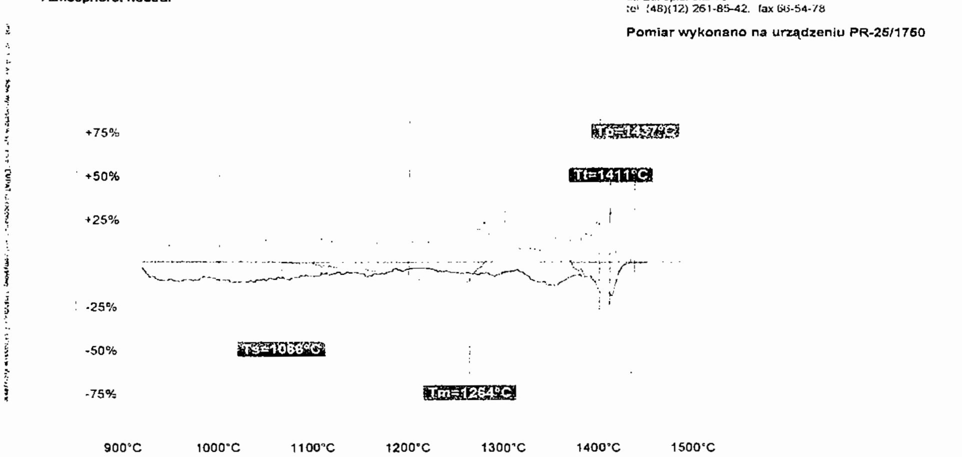
Komentarz:

Indeks: ii21AQ00

Foundry Research Institute
Zakład Technologii

Zlecenie: 2004_12_9 **Materiał: popiol_01**
Atmosphere: neutral

30-418 KRAKOW
ul. Zakopiańska 73
tel. (48)(12) 261-85-42, fax 66-54-78
Pomiar wykonano na urządzeniu PR-25/1750



Komentarz:

Fig.3.8. Thermal behavior of the Eastlake Plant fly ash with characteristic points

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30-418 KRAKÓW
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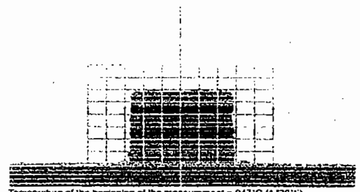
tel. (48)(12) 261-85-42, fax 66 54 78
Pomiar wykonano na urządzeniu PR-25/1750

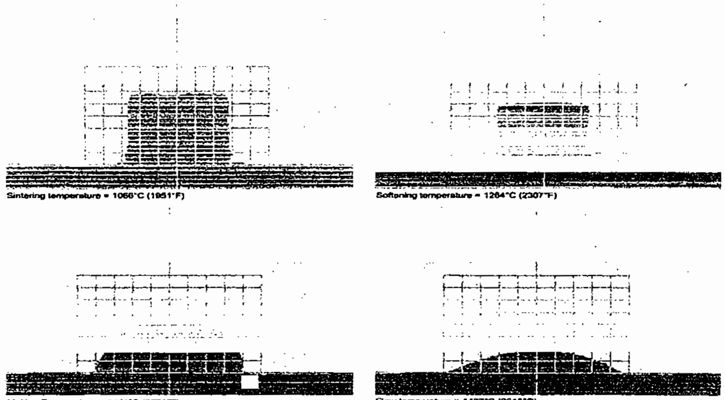
Indeks: ii21AQ00

Zlecenie: 2004_12_9
Materiał: popiol_01
Atmosphere: neutral

Sintering temperature = 1066°C (1951°F)
Softening temperature = 1264°C (2307°F)
Melting Temperature = 1411°C (2571°F)
Flow temperature = 1437°C (2618°C)



Temperature of the beginning of the measurement = 947°C (1736°F)



Sintering temperature = 1066°C (1951°F)
Softening temperature = 1264°C (2307°F)
Melting Temperature = 1411°C (2571°F)
Flow temperature = 1437°C (2618°C)

Komentarz:

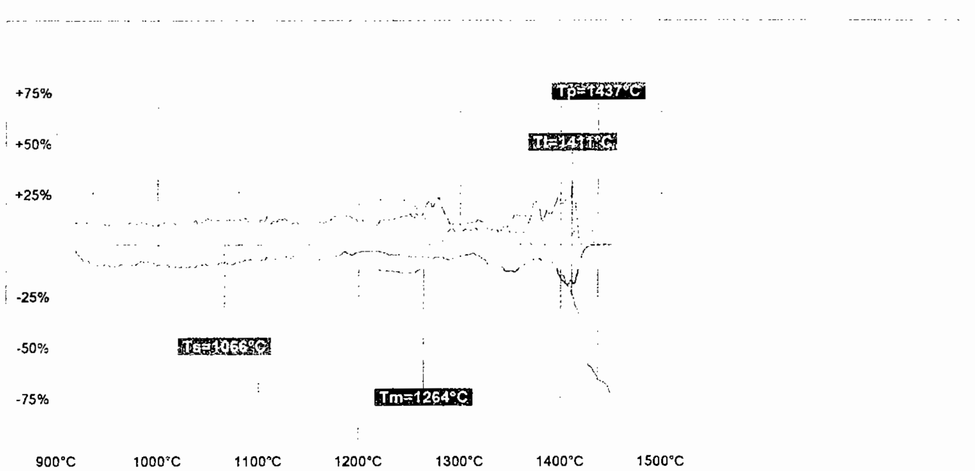
Indeks: ii21AQ00

Foundry Research Institute
Zakład Technologii

Zlecenie: 2004_12_9
Atmosphere: neutral

Materiał: popiol_01

30-418 KRAKÓW
ul. Zakopiańska 73
tel. (48)(12) 261-85-42, fax 66-54-78
Pomiar wykonano na urządzeniu PR-25/1750



Komentarz:

Fig.3.9. Thermal behavior of the Skawina fly ash with characteristic points

Table 3.3 Characteristic temperatures of investigated materials

Temperatures		Materials		
		Eastlake Plant fly ash	Skawina fly ash	Quartz sand
Sintering temperature	°C	1217	1066	-
	°F	2223	1951	-
Softening temperature	°C	-	1264	-
	°F	-	2307	-
Melting temperature	°C	1310	1411	1710 - 1713
	°F	2390	2571	3115 - 3145
Flow temperature	°C	1345	1437	-
	°F	2453	2618	-

Skawina fly ash showed lower sintering temperature; the other characteristic temperatures are significantly higher (app. 100^{0}C) than Eastlake Plant fly ash, but much lower, when compared to quartz sand or even the Dayton Power & Light material used on the previous project which was only slightly lower than quartz sand. The differences between the two fly ashes used on this project and those on the previous project are, most probably, the result of its chemical composition.

Both the examined mixtures reveal, starting with the temperature of about 1200^{0}C (2190^{0}F), some easily noted changes in volume. The observed effect of changes in dimensions is most likely related to a process of thermal degradation of the fly ash.

Toxicity

Starting in 1994, all waste disposed at landfills and/or utilized in various sectors of the industry (e.g. in highway construction or in mining) within Poland must meet certain requirements that are intended to protect the natural environment. These requirements are enforced through a series of Building Regulations that require all construction projects (including roads, landfills, etc.) to be environmentally safe and not toxic to the air, water, and soil and to therefore, have a full series of testing performed for determining the content of natural radioactive elements and for any other respective water born extracts that are possible from the materials being used. The main aspect of the testing is to determine the content of ions and noxious elements contained in the materials. The procedures followed in determining these threshold limit values, outlined below, were used to establish a baseline for the fly ash being tested.

The Table also includes the respective values obtained for water extracts prepared with the examined fly ash, with the fly ash-to-water mass ratio being 1: 10.

The analysis was made using the method of atomic absorption spectroscopy and atomic emission spectroscopy induced by a plasma (argon) jet on ICP MS ELAM 6100 and ICP AES Plasma apparatus.

Table 3.4 The results of analysis of the content of some selected pollutants in water extracts of the examined fly ashes

Type of pollutant	Unit	Threshold limit values	E.P.	Skawina
pH	----	6.5-9.0	11.49	12.01
Sulfides	mg SO_4/dm^3	500	573.7	202.1
Calcium	mg Ca/dm^3	not standardized	267.4	310.2
Chromium	mg Cr/dm^3	0.500	0.304	0.135
Cadmium	mg Cd/dm^3	0.100	0.00050	0.00250
Lead	mg Pb/dm^3	0.500	0.00016	0.00045
Arsenic	mg As/dm^3	0.200	0.00158	0.00200

The data given in this table indicates that when using a standard environmental threshold table. the fly ashes characterized exceed the admissible by pH value levels, which commonly occurs in these types of fly ash. The concentration of sulfate ions for the EP fly ash also exceeds the admissible threshold limit values. This is also typical of fly ash, especially those resulting from the combustion of brown coal burnt in fluidal-bed furnaces.

It should be noted, however, that in respect to the content of the selected heavy metals, the examined fly ashes are to be considered to be fully safe.

Natural radioactivity

In accordance with the recommendations issued by the Institute of Building Engineering, the indices for the level of radioactive pollutants f_1 and f_2 should meet the inequalities:

$$f_{1max} = f_1 + \Delta f_1 \leq 1$$

and

$$f_{2max} = f_2 + \Delta f_2 \leq 185 \text{ Bq/kg* and 200B q/kg**}$$

The respective measurements were taken by the semi-conductor gamma-ray spectrometry.

Based on the calculated concentration values of natural isotopes ^{40}K, ^{226}Ra and ^{232}Th, the index of radioactive pollutants for the tested fly ash was determined as:

Table 3.5 Natural radioactivity of the examined fly ashes

Coefficient of natural radioactivity	E.P.	Skawina
f1 [-]	$0.80^{\pm 0.02}$	$1.03^{+0.03}$
f2 [Bq/kg]	$90^{\pm 3}$	11^{+4}

Thereby indicating that the tested fly ashes are suitable for fabrication of materials used in construction of habitable buildings, or are otherwise considered as safe materials.

4. Preliminary trials on the choice of binding systems

The selection of the most optimum binding systems was achieved by considering both the fly ash medium being studied and the need to meet satisfactory strength properties with the proper permeability to permit the free passage of gas.

Because of the low values of permeability in foundry FASANDs (Fly Ash Sands) based on its type of granular make-up, inorganic and organic systems were studied. Inorganic binders, contrary to organic binders, are characterized by a very low gas evolution rate during the process of thermal decomposition. Of particular interest was finding an system that optimized the permeability of the fly ash as being as close to that found in traditional natural sands through a series of tests and trials.

The trials were conducted on the following organic binder systems:

1. Sodium silicate of modulus M = 2,1, density at 20^{0}C ρ = 1,520 g/cm^3 and absolute viscosity 50,0 cP, modified chemically with organofunctional, morphoactive additives, hardened thermally and chemically by ethylene glycol diacetate.

2. Hydrolyzed ethyl silicate „40", hardened with aqueous solution of ammonium hydroxide NH_4OH of 5% concentration

3. Portland cement.

As pore-forming additives the following were used:

1. Composition of various chemical compounds of the trade name Genifor GK-B,
2. Acid sodium carbonate $NaHCO_3$.

The use of ethyl silicate „40" as a binder required hydrolysis. The process of hydrolysis consisted in mixing 800 cm^3 of ethyl alcohol with 1907 cm^3 of ethyl silicate. To this obtained colloid, 304 cm^3 of distilled water and 3 cm^3 of concentrated HCl were added. The whole batch was stirred for the time necessary to reach maximum temperatures for the reaction of hydrolysis; in this particular case it was a time of 32 minutes. After a notable drop of temperature, 1530 cm^3 of ethyl silicate „40" was added to the stirred solution, and stirring of the whole batch was then continued for 15 minutes. The obtained binder was subjected to the process of natural ageing for 24 hours. Next, the applicability of the binder was tested. The test consisted of determining the gelling time. For this purpose, up to 100 ml of the binder was added to 5 ml of aqueous solution of ammonium hydroxide of a 5% concentration. The gelling time of the binder was 3 – 4 minutes.

Trials were conducted on foundry samples of the following compositions (in parts by weight):

1. fly ash - 100,0
   sodium silicate - 10, 12, 14, 18
   diacetate of ethyle glycol - 15% in respect of sodium silicate
2. fly ash - 100,0
   sodium silicate - 10, 12, 14
   Genifor GK-B - 1,5%, 5%, 15%, 30% in respect of fly ash
3. fly ash - 100,0
   sodium silicate - 10, 12, 14
   $NaHCO_3$ - 1,5%, 5%, 15%, 30% in respect of fly ash
4. fly ash - 100,0
   ethyl silicate „40" - 40,0
   NH_4OH - 5% in respect of ethyl silicate „40"
5. fly ash - 100,0
   ethyl silicate „40" - 40,0
   silica sand - 0,20/0,32/016 = 7 : 3
   NH_4OH - 5% in respect of ethyl silicate „40"
6. fly ash : molochite = 7 : 3 - 100,0
   ethyl silicate „40" - 40,0
   NH_4OH - 5% in respect of ethyl silicate „40"
7. fly ash - 100,0
   Portland cement - 25,0
   water - 12,5
8. fly ash - 100,0
   Portland cement - 25,0
   water - 25,0
9. fly ash - 100,0
   Portland cement - 50,0
   water - 25,0

5. Testing the technological properties of produced foundry sands

Foundry sands of the compositions as stated above were prepared in a standard laboratory mill, type LMR-1 (Fig.5.1); the cylindrical specimens were made on a standard automatic rammer, type LUA (Fig.5.2).

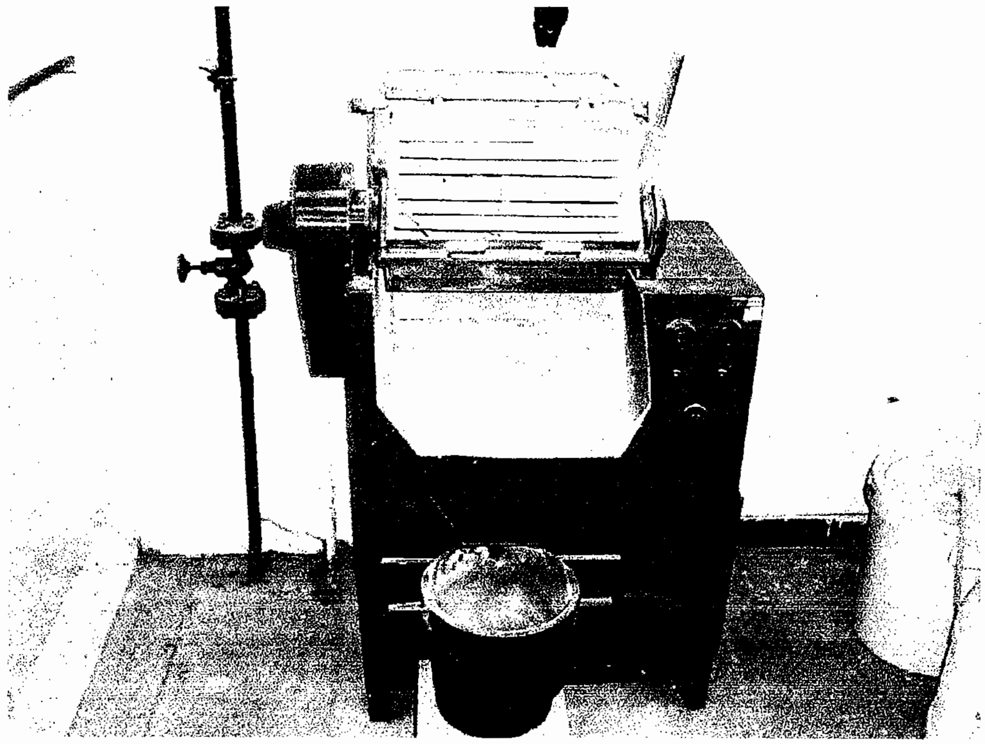


Fig.5.1. Standard ribbon sand mill, type LMR-1

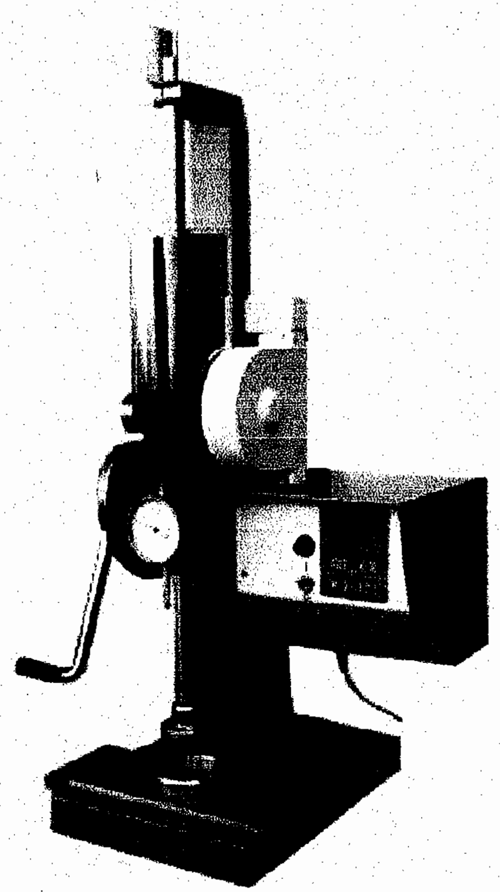


Fig.5.2. Standard rammer, type LUA-2e

In the case of sample no. 1, the fly ash was mixed with ethylene glycol diacetate for 4 minutes, followed by addition of sodium silicate and mixing the whole batch for the next 4 minutes. In the case of samples nos. 2, 3, 7, 8 and 9, the fly ash was mixed with an addition of Genifor GK – B or with $NaHCO_3$ for 4 minutes; then sodium silicate was added, and the whole was mixed for the next 4 minutes. Foundry samples nos. 4, 5 and 6 were made in a typical Shaw Process.

The hardening process of foundry samples were as follows:

sample no. 1 – hardened at ambient temperature due to chemical reactions taking place between sodium silicate and ethylene glycol diacetate,

sample nos. 2 and 3 - thermal treatment at 145^0C for 3 hours,

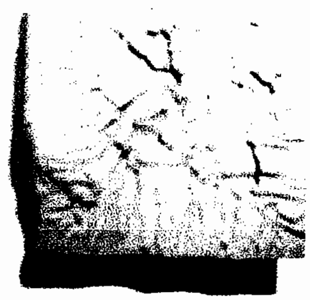
sample nos. 4, 5 and 6 – after hardening the samples were baked to remove ethyl alcohol. After cooling, the samples were tested before the process of thermal treatment and after this process, i.e. after holding for 1 hour at temperatures from ambient temperature to 900 ^{0}C.

Sample nos. 7, 8 and 9 - hardened at ambient temperature as a result of hydratation of silicates and calcium aluminates.

The results of the mechanical tests and permeability measurements taken on the specimen samples prepared from foundry samples nos. 1 - 9 are given below:

1. Sample no. 1 - mean values of compression strength and permeability after 24 hour hardening amounting to R_c^{24} = 0,7 MPa and $P^{24} = 7 \cdot 10^{-8}$ $m^2/Pa \cdot s$, respectively, were obtained by adding 14 parts by weight of sodium silicate. Lower content of sodium silicate was not sufficient to confer to the specimens the required shape resistance. Typical fractures of the sample specimens are shown in Figure 5.3a.

a



b

Fig.5.3. Typical fractures of specimens made from foundry sample nos. 1 (a) and 4b (b). Note in Figure b the network of interconnected passages, very effective for rendering a way for the gas flow

2. Sample nos. 2 and 3 – increasing the content of Genifor GK-B and $NaHCO_3$ to more than 5% in respect of the fly ash content caused a rapid drop in the strength properties in these foundry samples, irrespective of the addition of sodium silicate. With the above mentioned additives introduced in an amount of 5% and with 14 parts by weight of the binder (sodium silicate), the following mean values of compression strength R_c^{24} and permeability P^{24} after 24 hour hardening were obtained: with Genifor GK-B: R_c^{24} = 0,79 MPa and $P^{24} = 6 \cdot 10^{-8}$ $m^2/Pa \cdot s$, and with an addition of $NaHCO_3$: R_c^{24} = 0,79 MPa and $P^{24} = 10 \cdot 10^{-8}$ $m^2/Pa \cdot s$
3. Sample no. 4 – mean compression strength and permeability before the thermal treatment (sample no. 4a) were: R_c^{24} = 0,47 MPa and $P^{24} = 24 \cdot 10^{-8}$ $m^2/Pa \cdot s$, respectively; after the thermal treatment (sample no. 4b) those values were: R_c^{24} = 0,67 MPa and $P^{24} = 80 \cdot 10^{-8}$ $m^2/Pa \cdot s$,

respectively. Typical fracture of the specimen made from sample no. 4b is shown in Figure 5.3b.

4. Sample no. 5 - mean compression strength and permeability before the thermal treatment (sample no. 5a) were: $R_c^{24} = 1{,}0$ MPa and $P^{24} = 19 \cdot 10^{-8}$ $m^2/Pa \cdot s$; respectively; after the thermal treatment (sample no. 5b) those values were: $R_c^{24} = 1{,}04$ MPa and $P^{24} = 73 \cdot 10^{-8}$ $m^2/Pa \cdot s$, respectively.
5. Sample no. 6 - mean compression strength and permeability before the thermal treatment (sample no. 6a) were: $R_c^{24} = 0{,}68$ MPa and $P^{24} = 15 \cdot 10^{-8}$ $m^2/Pa \cdot s$, respectively; after the thermal treatment (sample no. 6b) those values were: $R_c^{24} = 0{,}80$ MPa and $P^{24} = 60 \cdot 10^{-8}$ $m^2/Pa \cdot s$, respectively.
6. Sample no. 7 - mean compression strength and permeability after 24 hour hardening were: $R_c^{24} = 0{,}62$ MPa and $P^{24} = 4 \cdot 10^{-8}$ $m^2/Pa \cdot s$, respectively; after 48 hour hardening those values were: $R_c^{48} = 0{,}86$ MPa and $P^{24} = 4 \cdot 10^{-8}$ $m^2/Pa \cdot s$, respectively.
7. Sample no. 8 - mean compression strength and permeability after 24 hour hardening were: $R_c^{24} = 0{,}68$ MPa and $P^{24} = 5 \cdot 10^{-8}$ $m^2/Pa \cdot s$, respectively; after 48 hour hardening those values were: $R_c^{48} = 1{,}16$ MPa and $P^{24} = 5 \cdot 10^{-8}$ $m^2/Pa \cdot s$, respectively.
8. Sample no. 9 - mean compression strength and permeability after 24 hour hardening were: $R_c^{24} = 1{,}27$ MPa and $P^{24} = 4 \cdot 10^{-8}$ $m^2/Pa \cdot s$, respectively; after 48 hour hardening those values were: $R_c^{48} = 2{,}60$ MPa and $P^{24} = 5 \cdot 10^{-8}$ $m^2/Pa \cdot s$, respectively.

The results of the tests are shown in Figure 5.4.

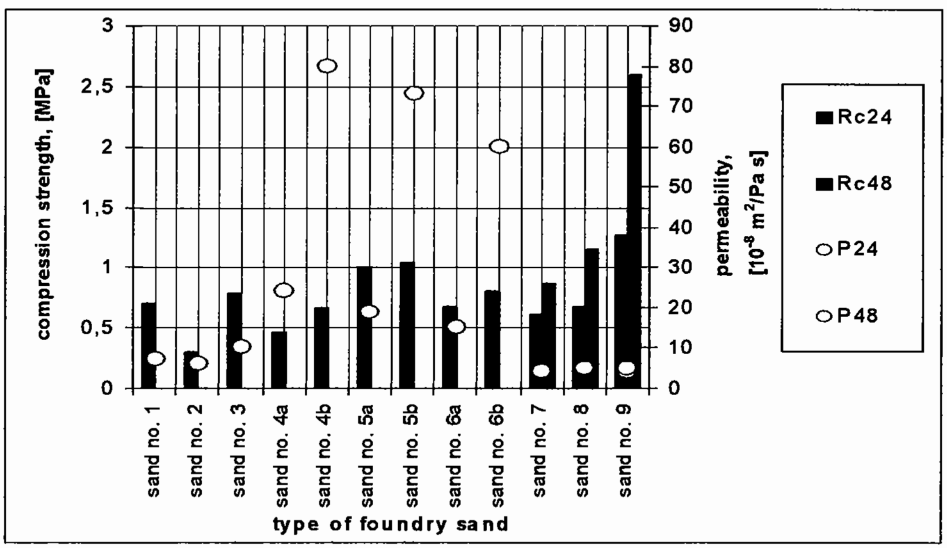


Fig.5.4. Compression strength after 24 hours (Rc24) and 48 hours (Rc48) and permeability after 24 hours (P24) and 48 hours (P48) of foundry sand specimens made from the fly ash-based mixture

Basing on the results of the tests, the following conclusions were formulated:

1. The compression strength Rc^{24} of samples nos. 1 - 9 did not exceed the value of 1.3 MPa, maximum values being obtained in foundry samples nos. 9, 5a and 5b. In the case of foundry samples nos. 7, 8 and 9, a considerable increase of compression strength after 48 hour hardening was obtained. In comparison with the compression strength of foundry samples nos. 7, 8 and 9, after a 24 hour hardening the increase amounted to approx. 40, 70 and 100%, respectively.
2. The addition of pore-forming agents (Genifor GK-B and $NaHCO_3$) was not sufficiently effective to produce the required open porosity in the foundry samples (samples nos. 2 and 3), and as such had no beneficial effect on their permeability.
3. The permeability of foundry samples nos. 1, 2, 3, 4a, 5a, 6a, 7, 8 and 9 was very low, i.e. up to $30 \cdot 10^{-8} \cdot m^2/Pa \cdot s$. The highest values of the permeability (from about 80 up to about $60 \cdot 10^{-8} \cdot m^2/Pa \cdot s$) were obtained in foundry samples nos. 4b, 5b and 6b.

6. Technical trials on the application of new molding "sands" or FASANDs in the production of iron castings under EIO and FRI conditions

At the foundry of Energy Industries of Ohio (Metal Casting Development Center in Cleveland, Ohio), trials were made on casting gray iron to sand molds bonded with CO_2-hardened sodium silicate binder. In these molds, cores made from the fly ash mixture according to formula 1 (sample no. 1) were placed as shown in (Fig. 6.1 a, b). The pouring temperature was 1420^{0}C (2588^{0}F). The successive stages of the pouring process are shown in Fig. 6.2 (a – g).

a b

Fig. 6.1. Cores in preparation (a) ; ready core made from a Eastlake fly ash (b)

a b

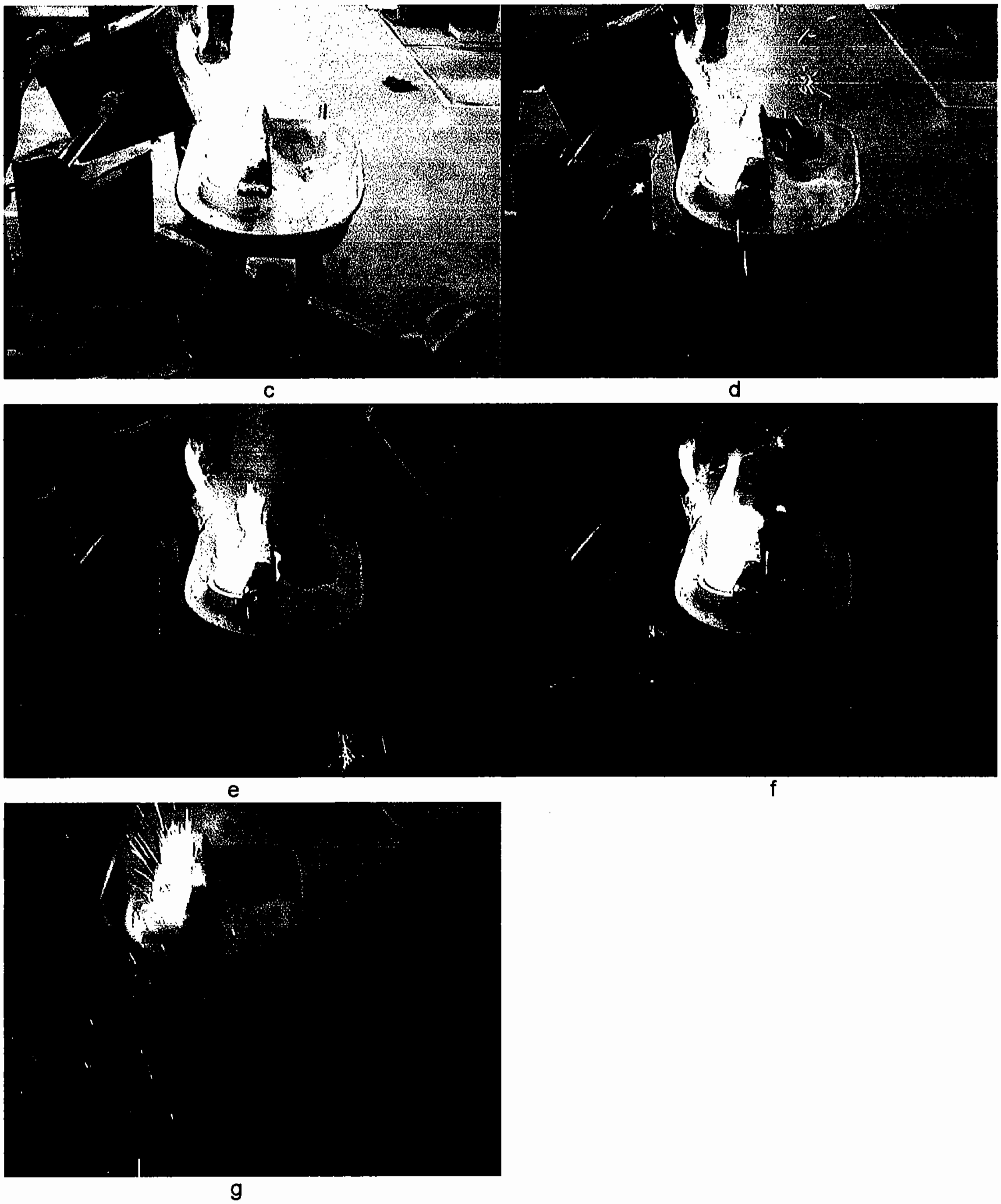
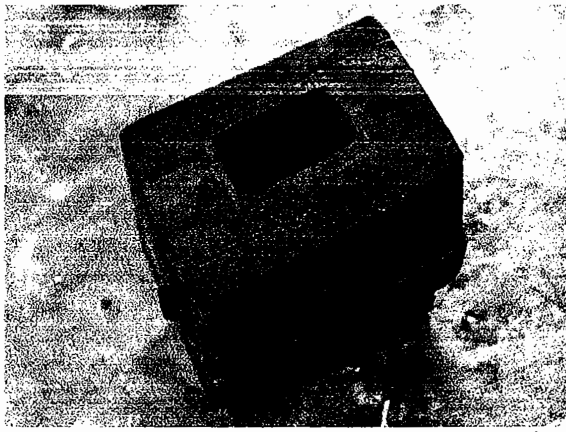
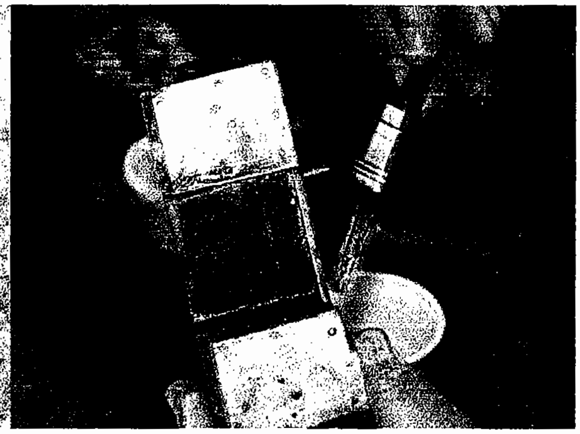


Fig. 6.2. The successive stages of pouring with gray iron molds with FASAND cores made from an Eastlake FASAND core (a-g)

In a foundry at the Foundry Research Institute - Krakow, trials were made on pouring of ductile iron into bentonite sand molds, in which cores made from the fly ash mixture according to formulae no. 1, 4 and 7 (samples nos. 1, 4, 7) were placed as shown in (Fig. 6.3 a – b). The pouring temperature was 1450^{0}C (2642^{0}F). The successive stages of the pouring process are shown in Fig. 6.3 i – l.

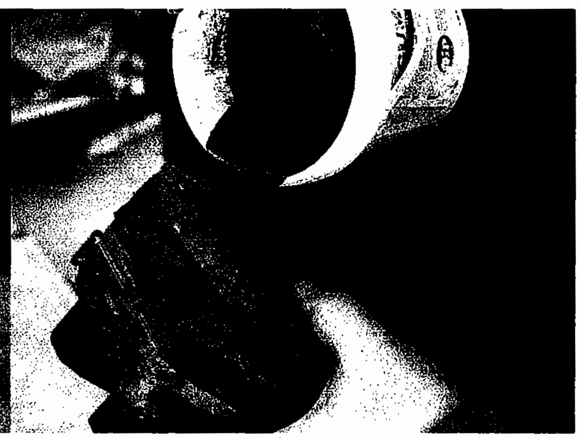


a



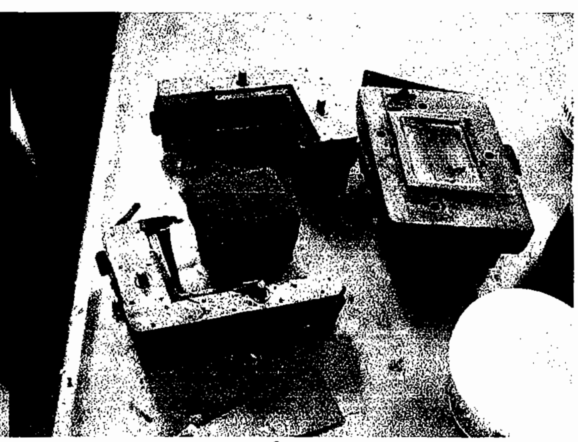
b

c



d

e



f

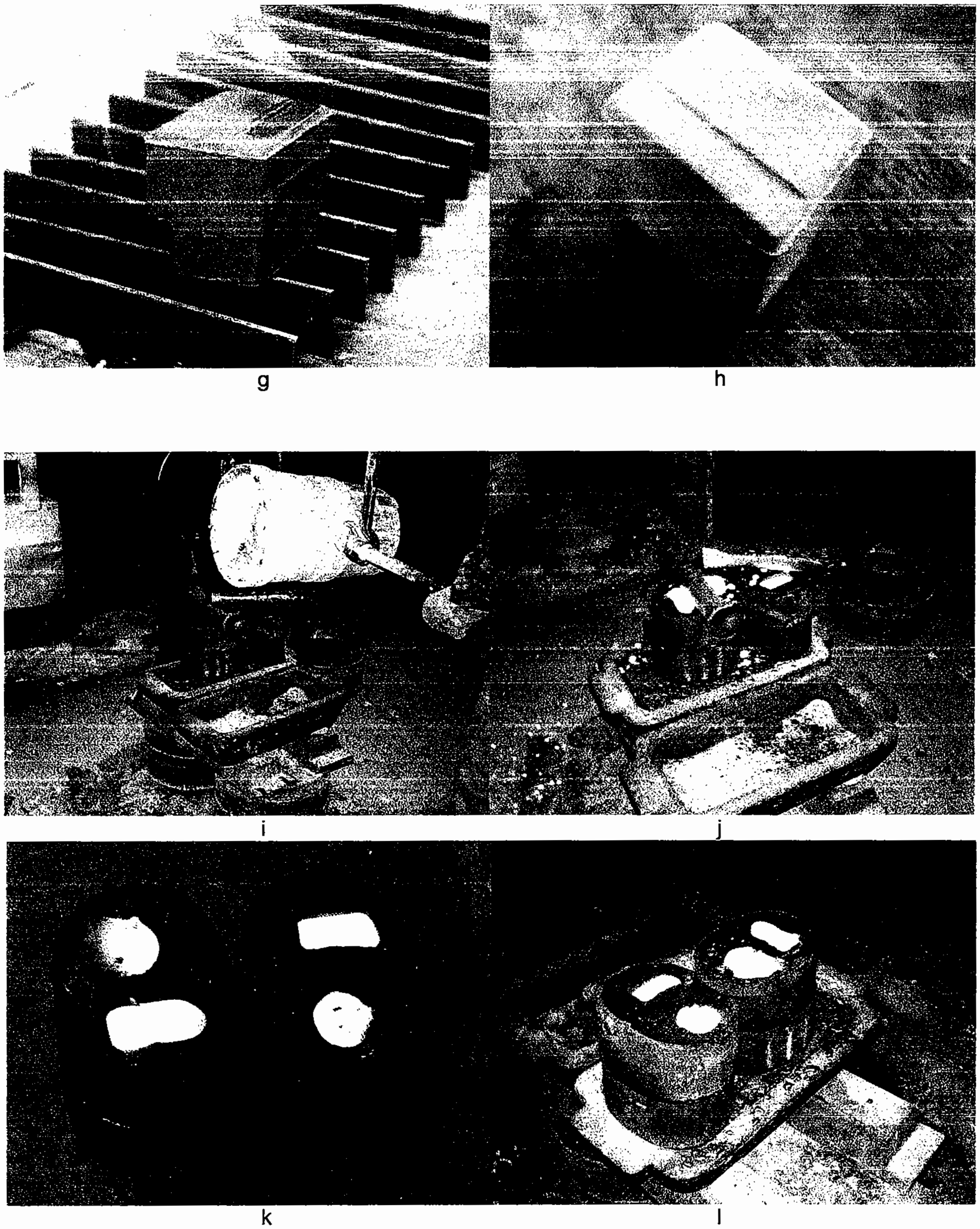


Fig. 6.3 (a – l). The successive stages of making core and pouring it with cast iron in bentonite sand molds (on the example of sand no.4 made from Eastlake Plant fly ash)

Trials were also conducted on pouring of ductile iron into the sodium silicate bonded, CO_2-hardened sand molds, in which cores made from the fly ash mixture according to formula no. 7 were placed (Fig. 6.4 a – b). The pouring temperature was 1450^{0}C (2642^{0}F). The successive stages of the pouring process are shown in Fig. 6.4 i – l.

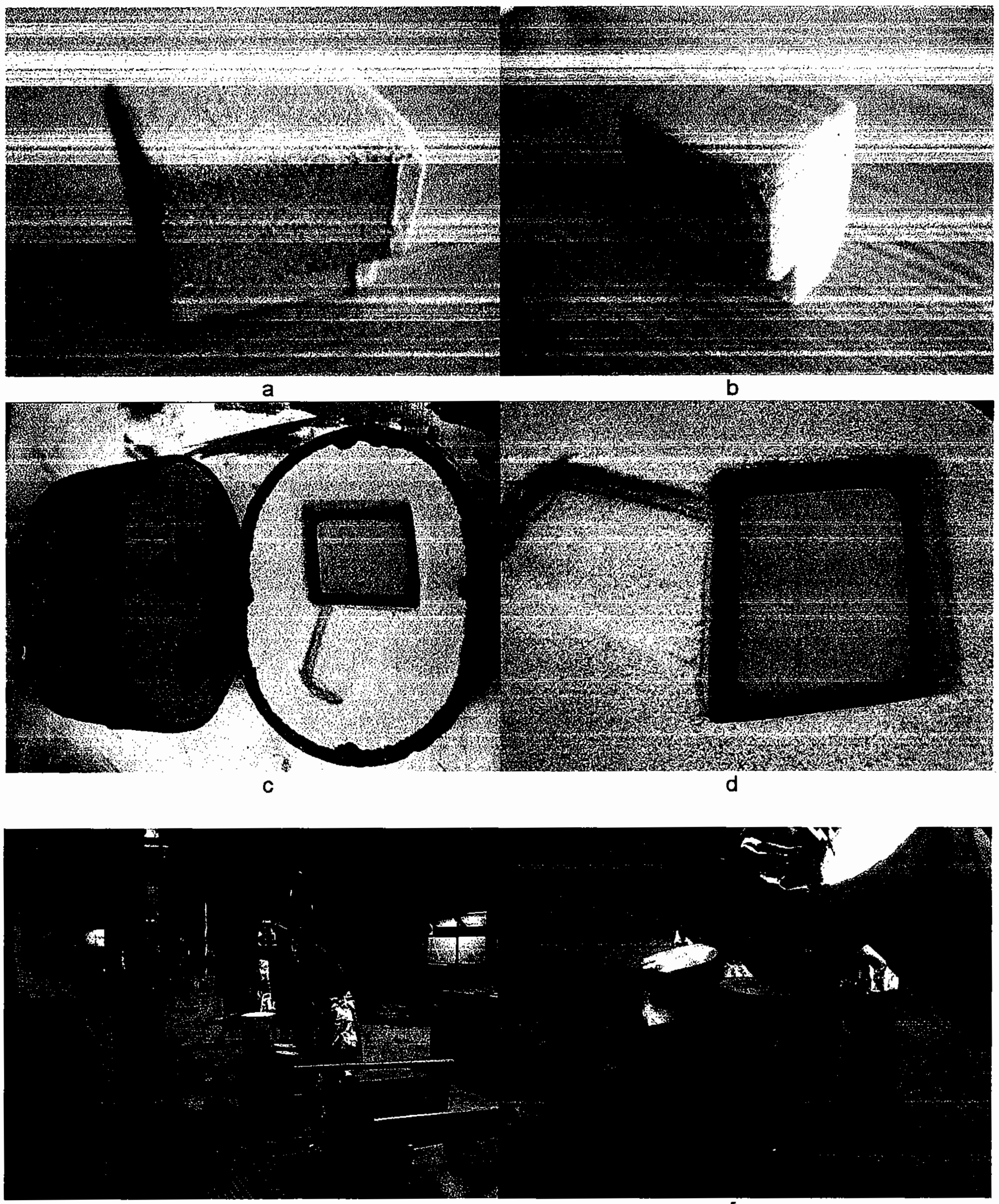


Fig. 6.4 (a – f). The successive stages of core preparation according to formula no. 7 (sand no.7, Eastlake Plant fly ash) and pouring of sand molds

7. Inspection of Castings

Tests made under EIO conditions at the Casting Development Center

The surface quality of castings reproduced by cores made from the Eastlake Plant fly ash mixture were satisfactory with exception of the areas which were affected by a high rate of gas evacuation (Figs.7.1-7.2). This referred especially to the zone of overflows and risers.

Fig. 7.1. Casting with well visible holes formed due to the high gas content

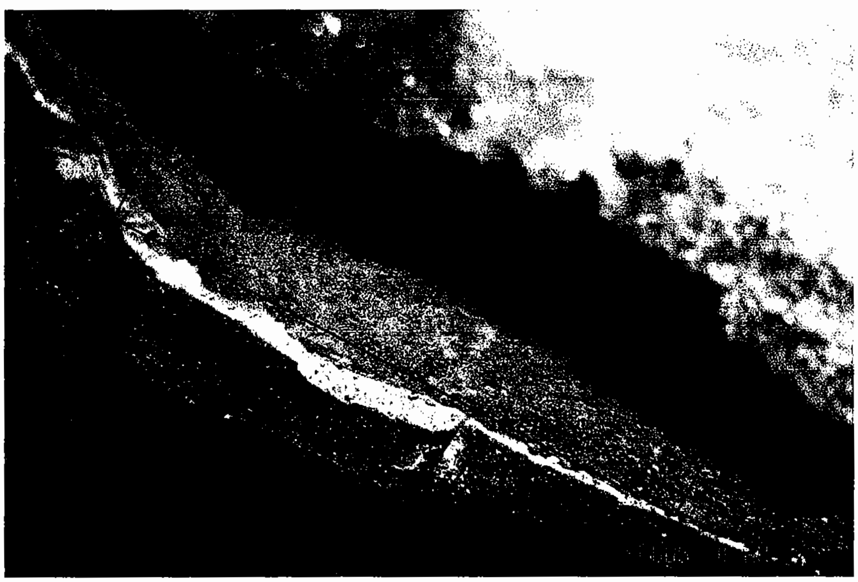


Fig. 7.2. Casting surface adjacent to the core made from a fly ash mixture (the area within a border red line)

Tests made under Foundry Research Institute conditions

Similar to the heats (pours) done at EIO, the castings made using cores of both Eastlake Plant and Skawina fly ash showed very satisfactory surface finishes except in those areas affected by gas releases. This is evident especially in the overflows and risers of the casting (Figs.7.3 – 7.10).

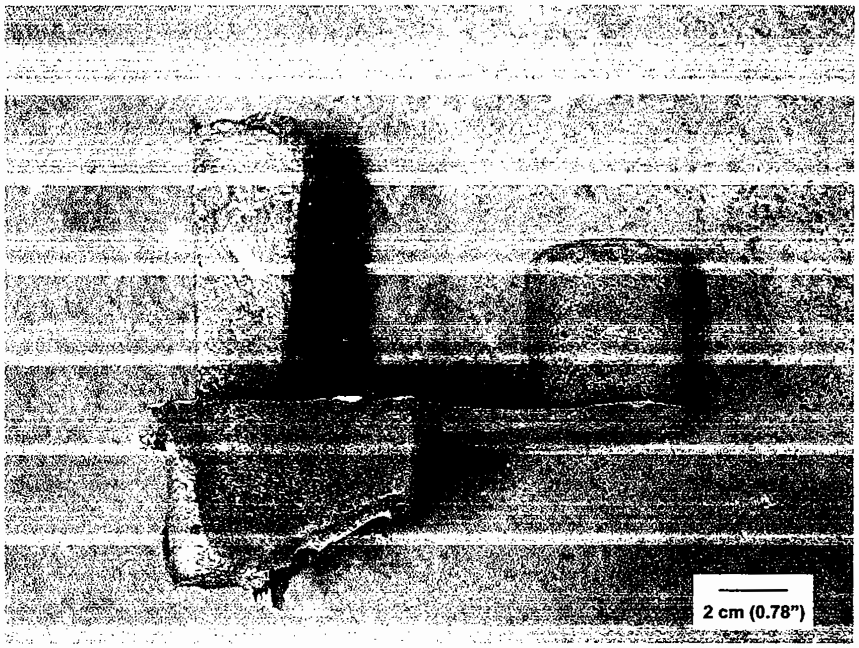


Fig. 7.3. Casting made from ductile iron with Eastlake Plant FASAND core

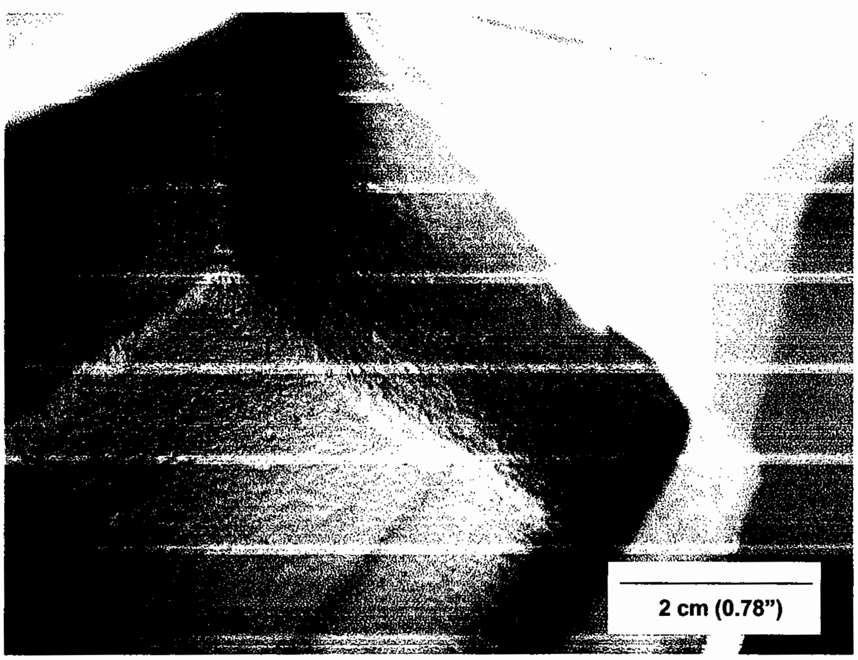


Fig. 7.4. A view of the casting surface from the side of core made from Eastlake Plant FASAND core

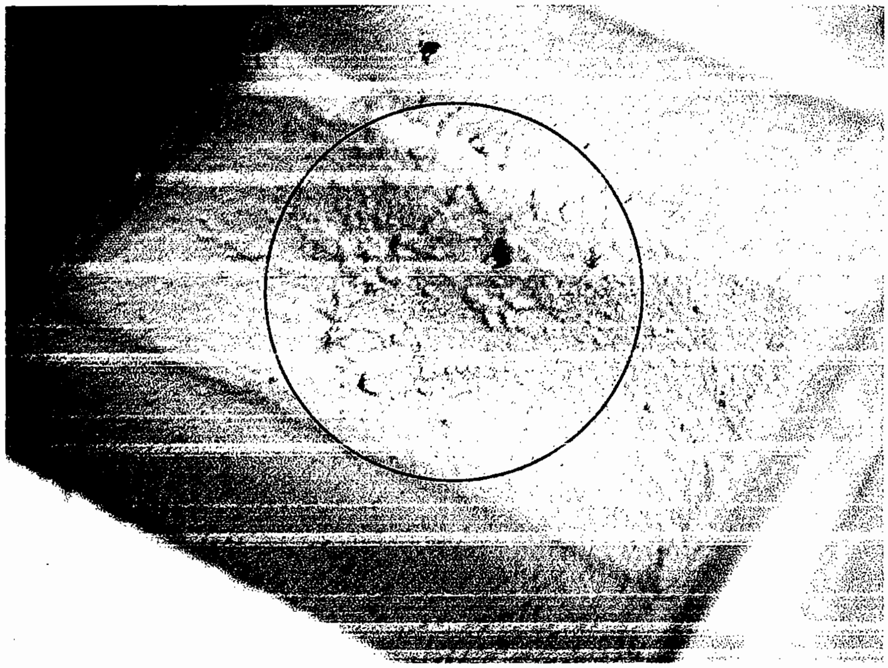


Fig. 7.5 Casting with small gas porosity (a hole) from the side of core made from Eastlake Plant FASAND (Shaw Process)

Fig.7.6. A view of the casting surface with well visible areas affected by gas porosity (Skawina FASAND core)

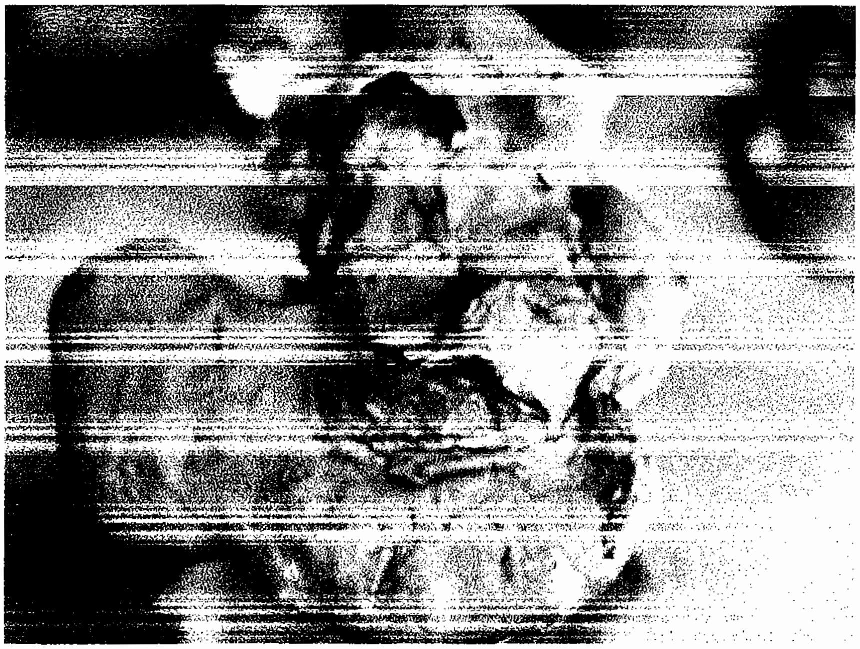


Fig. 7.7. Casting surface with areas affected by gas porosity (Skawina FASAND core)

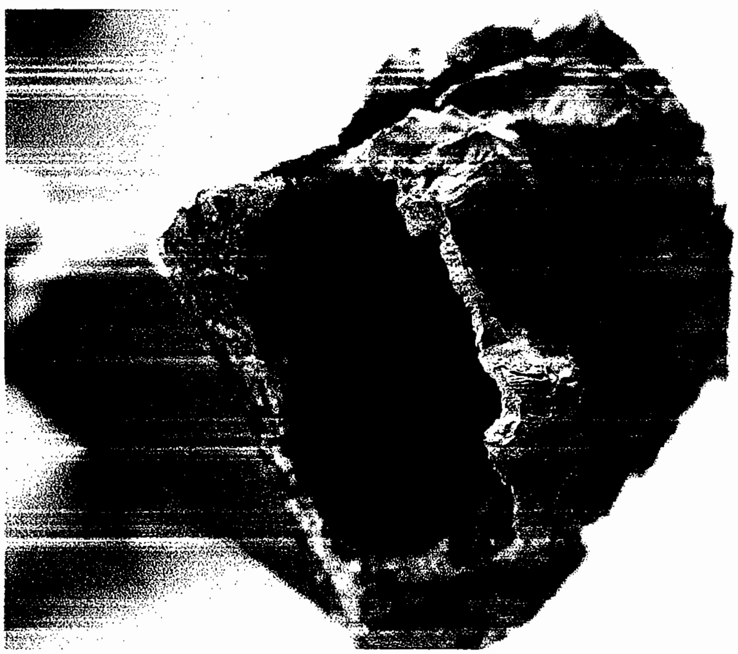


Fig. 7.8. Crater formed in the area of an overflow (Skawina FASAND core)

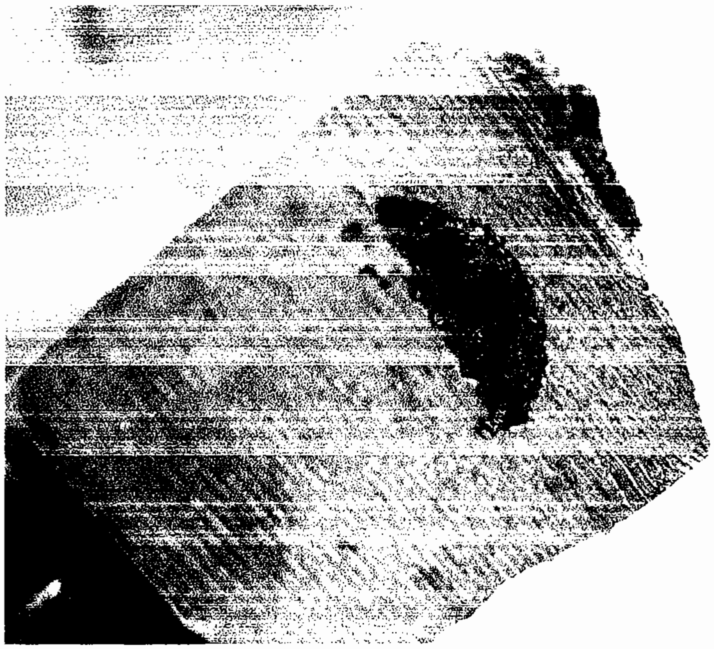


Fig.7.9. Cross-section of an overflow with well visible area of gas porosity (Eastlake FASAND core)

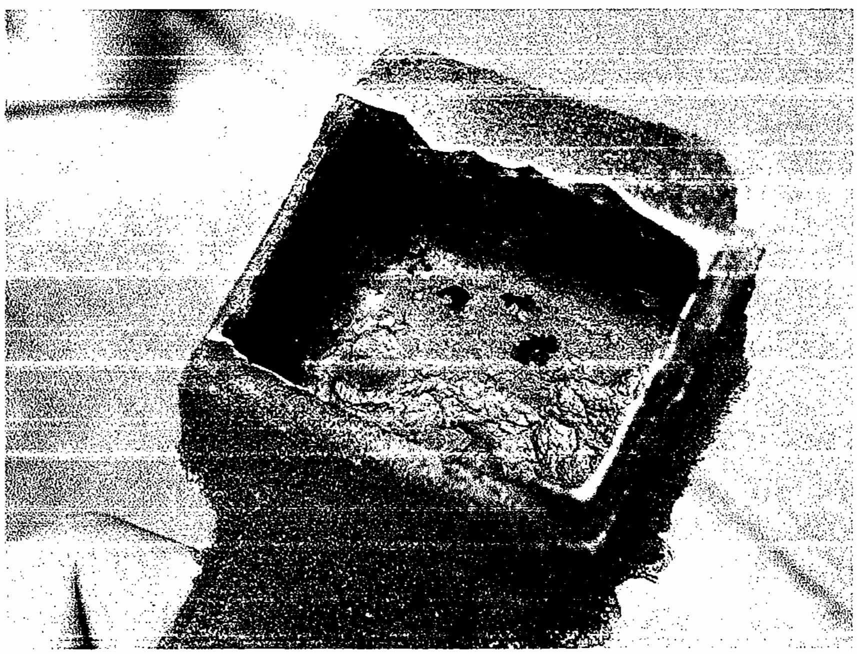


Fig. 7.10. Visible areas of gas porosity in the zone of gas escape to the overflow (Eastlake FASAND core)

8. Final Demonstration

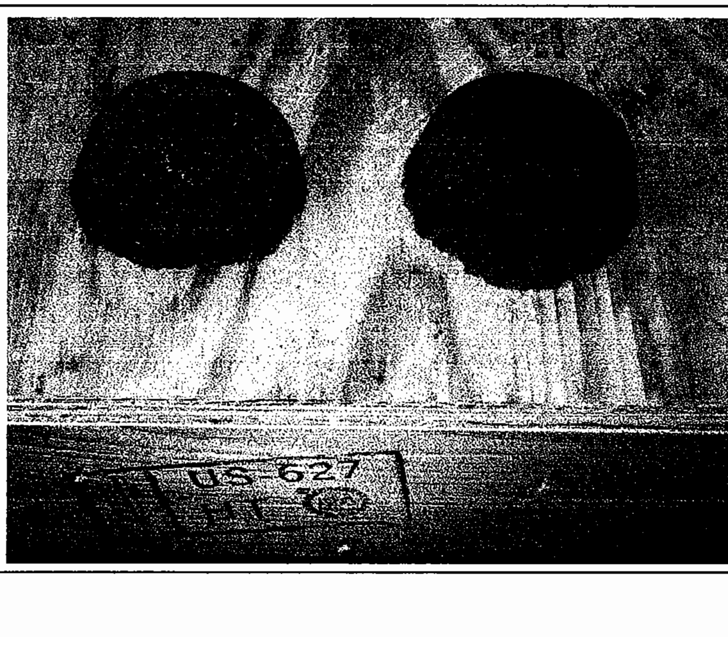
During October, 2005, a final demonstration for officials from General Motors took place at the Casting Development Center. Purpose of this demonstration was to test fly ash cores that had an Ashland Chemical proprietary coating applied as is currently used at the GM production plant. This test was to determine whether the coating would have an impact upon the test findings that were obtained during the above previously performed tasks.

Cores were prepared for being coated with both products (a green and pink type coating) that are used at the GM production facility. Dry Sand molds were prepared. Cores were made from EP type fly ash and were coated with both types of coating medium. They were permitted to cure. Both Aluminum and Iron was then poured into the sand molds fully covering the coated fly ash cores.

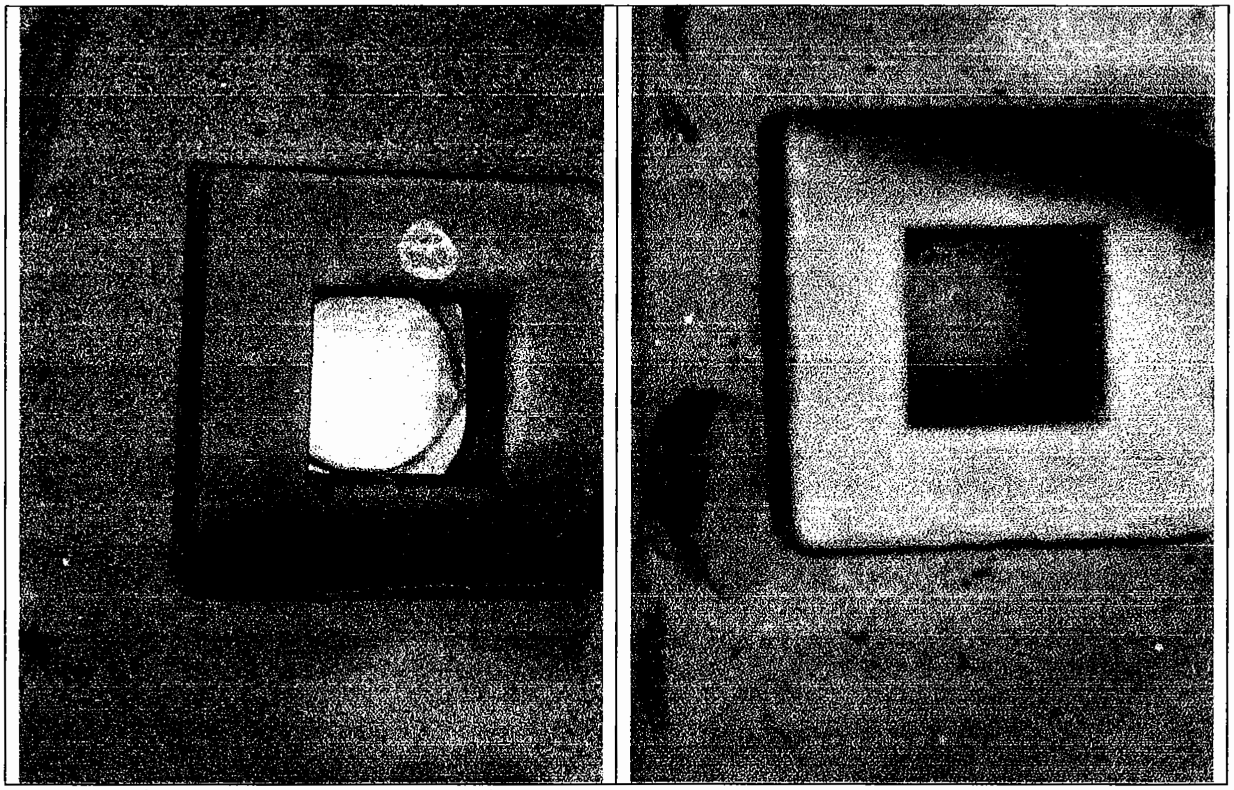
What was of significant importance was that the out-gassing noted in the earlier tasks did again appear to be a significant factor for these samples of fly ash being tested though only an inorganic binder was employed. The out-gassing, however, in this instance, appeared to be much more concentrated into a type of jet most likely caused at a fissure in the coating which acted as a relief zone for the trapped gas under the coating. □

It was determined that the fly ash medium, containing considerably higher concentrations of calcium and possibly unburned coal was again the main culprit for the out-gassing. Earlier assumptions that some of the out-gassing was also caused by the organic binder were somewhat challenged given the amount of out-gassing during the entire solidification process being very similar to that noted during the earlier trials.

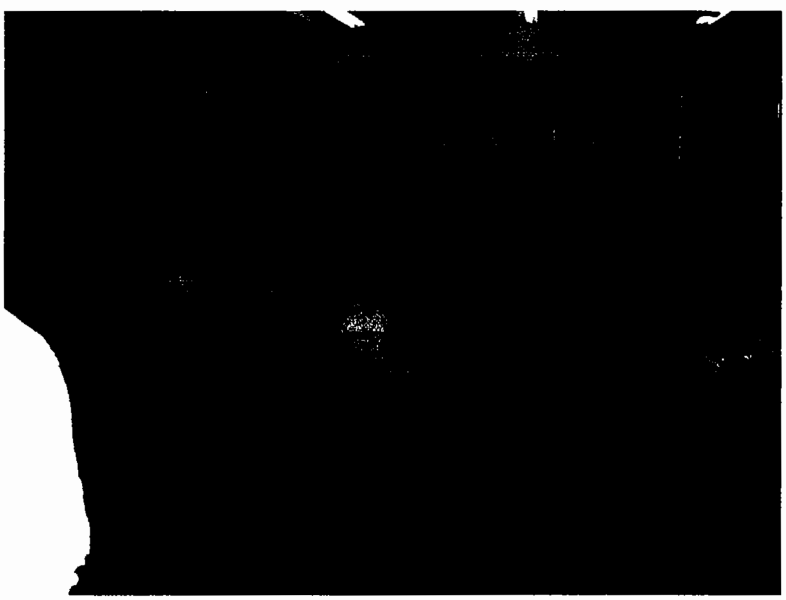
One significant outcome was the interest by the GM officials for the smooth surface finish of the cores being made using the fly ash. The challenge presented by those in attendance at the pour demonstrations was whether we could find the type of ash and binder system that would reduce the out-gassing while also afford itself to ease in break/shake out and remain having the smooth finish noted.



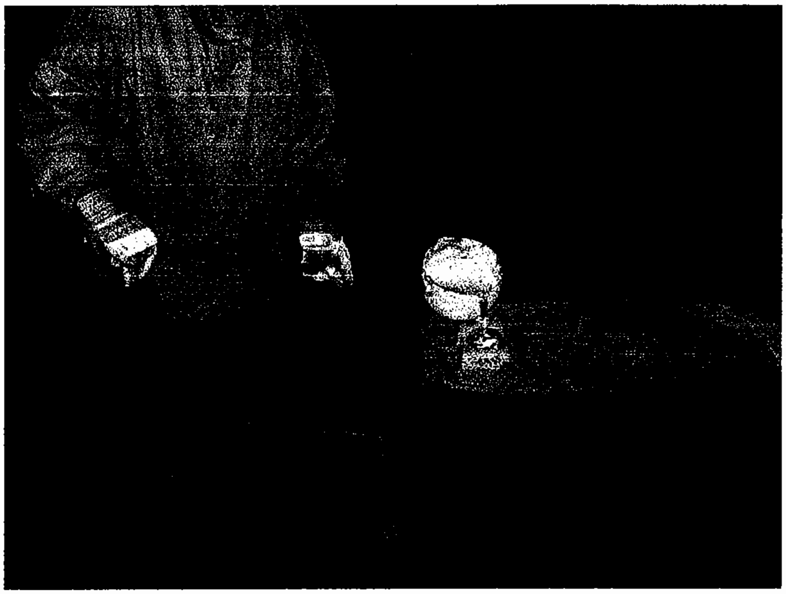
8.1 Sample Cores made from fly ash and sodium silicate binder



8.2 Cores with Blue and Pink Coating nested in dry sand molds prior to pour



8.3 Two Iron and Two Aluminum Molds were poured



8.4 Aluminum Molds were poured after the iron molds

8.5 Iron Molds after pouring. Note out-gassing on casting to right in a concentrated "jet"

CONCLUSIONS

9. FINAL CONCLUSIONS

1. The best among the proposed chemical compositions and fabrication methods of foundry molding and core mixtures based on 100% on fly ash (FASAND) type mixtures were considered as the following (the composition in parts and percent by weight):

- sample no. 1 (fly ash – 100.0; sodium silicate – 18; ethyl glycol diacetate - 15% in respect to the sodium silicate)
- sample no. 4 (fly ash – 100.0; ethyl silicate „40" – 40.0; NH_4OH - 5% in respect of ethyl silicate „40" – made by the Shaw process)
- sample no. 7 (fly ash – 100.0; Portland cement – 25.0; water – 12.5)

2. In the course of heating the samples of FASAND mixtures, starting with the temperature of about 1200^{0}C (2190^{0}F), there is a change in their volume which causes geometrical changes in the molds and/or cores, a consequence of which may be changes in the iron castings dimensions and geometry. The observed effect of the change of dimensions is most likely related to the process of thermal degradation of the fly ash thus indicating that only ashes that have high melting points are suitable for iron/ferrous castings.

3. The conducted technological trials demonstrated that all of the examined FASAND mixtures were characterized by a very high rate of gas evolution at the very moment of contact between the core and liquid cast iron, and that this effect persists throughout the whole process of iron casting solidification. The gas evolution rates (from the highest to the lowest) assumed the following sequence: sample no. 1 › sample no. 7 › sample no. 4. Another unfavorable effect was thought to be the low permeability of these mixtures; arranged according to the sequence "from the lowest to the highest" the order is: sample no. 1 › sample no. 7 › sample no. 4. HOWEVER, when performing the final demonstration of the process, GM noted that a low permeability was actually a desirable attribute of the mold medium as it might eliminate the need to coat the cores which is a costly and time (curing) consuming process.

4. The reason for the gas evolution rate being so high in the case of FASAND mixtures is believed due to the thermal decomposition of the binder (specially the residual water content) and, probably, the thermal degradation of the base material (fly ash) grains, due to the low softening and melting points. Contrasting the fly ash used in this particular set of evaluations it is noted that there exists a considerable difference to the ashes used in the prior analysis. The Dayton Power & Light ash appears to have a melting temperature just slightly lower than quartz sand. Another aspect of the attempted process that differs from the desired production site characteristics was the use of a combined inorganic/organic binder to achieve permeability. Given that the desire is to reduce permeability, a more suitable inorganic medium that will have considerably less off-gassing is contemplated for future trials at GM.

5. Even in view of the noted problems experienced during the project, and taking into consideration the results of the tests conducted so far and discussed in the previous report, the utilization of fly ash as a 100% - base granular material of foundry FASAND mixtures, especially if used for cores, continues to be recommended for castings made from non-ferrous metals with the temperature of pouring up to approx. 1200^0C (2190^0F).

6. Further studies on the practical applications of FASAND mixtures for the production of iron castings should be focused on further defining the types of fly ash suited to the high temperature ranges experienced in ferrous metal casting. These higher thermal characteristic ashes or optimizing less advantageous fly ashes by removing the low-melting point constituents or blending with quartz sand should be pursued.

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Appendix C

Final Report
00-CBRC-M04

Crushed Aggregates from Class C Fly Ash

Anil Misra, IP

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1. Document Title: "Crushed Aggregates from Class C Fly Ash" (Proj #98-166)

2. Type of Document: ☐ Technical Progress Report ☐ Topical Report ☒ Final Technical Report
☐ Abstract ☐ Technical Paper ☐ Journal Article ☐ Conference Presentation
☐ Other (please specify): ____

3. Date clearance needed: ____

♦4. Patent information.

Yes	No	
☐	☒	Is any patentable subject matter disclosed in the report?
☐	☐	If so, has an invention disclosure been submitted to DOE Patent Counsel? If yes, identify disclosure number or DOE Case Number ____
☐	☒	Are there any patent-related objections to the release of this report? If so, state the objections.

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B. DOE PATENT COUNSEL ACTION

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CRUSHED AGGREGATES FROM CLASS C FLY ASH

Draft Final Report

to

Combustion Byproducts Recycling Consortium

West Virginia University

by

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October 31, 2005

TABLE OF CONTENTS

I. INTRODUCTION AND EXECUTIVE SUMMARY

Self-cementing class C fly ash is produced in voluminous quantities by utilities in the Midwest as a result of burning sub-bituminous coal from Wyoming. Owing to their self-cementing nature, these fly ashes may be used as cement surrogates. In the proposed research project, the self-cementing nature of these fly ashes is exploited to develop lightweight aggregates that may be used for a wide variety of construction activities.

Hydrated class C fly ash can have compressive strength comparable to low-strength rocks. For example, 7-day air cured samples of class C fly ash-sand mortar have compressive strengths of 10 MPa and above. Furthermore, compressive strengths of some hydrated class C ashes have been reported to be as high as 15 MPa with a specific gravity of less than 2.0. Moreover, additives such as kiln dust, lime and fibers may enhance the strength and other mechanical properties of hydrated class C fly ash. This indicates that class C fly ash could be used to produce lightweight aggregates that would classify as low-strength rocks and could be used as granular base course for highways, as backfill behind retaining structures, as decorative rocks, in specialty concrete, and in other applications. In addition, hydrated class C ponded ash may also be reclaimed from ponds to produce crushed aggregates.

In this research project, we have evaluated class C fly ash aggregates produced by: (1) extruding laboratory cured mixtures of water, class C fly ash, fibers and sand, (2) crushing laboratory cured mixtures of water and class C fly ash, and (2) crushing reclaimed hydrated ponded class C fly ash. A variety of tests were performed to characterize the physical and engineering properties of these aggregates, including particle shape, surface texture, moisture absorption capacity, specific gravity, density, soundness, and durability. The engineering properties of these aggregates for application as pavement base course material, as backfill material and as embankment materials were evaluated by investigating their compaction behavior, and California Bearing ratio (CBR).

This report describes the findings of the research project related to: (1) the literature review of fly ash aggregates and use of fibers in cementitious products, (2) the physical and chemical characteristics of class C fly ash, (3) the determination of optimal ash-sand proportion and optimal ash-fiber-sand mixes, (4) aggregate production and characterization, and (5) ponded ash aggregate characterization. Based upon the results of this research, we find that aggregates produced by exploiting class C fly ash self cementing property have characteristics that are best suited for applications such as road bases, lightweight embankment fills or lightweight granular backfills behind retaining walls. Therefore, ponded class C fly ashes could yield a rich source of crushed aggregates that may be used for these construction applications.

II. LITERATURE REVIEW OF FLY ASH/SYNTHETIC AGGREGATES

The literature review was performed with a focus upon collecting, reviewing, analyzing and summarizing available information concerning: (1) the utilization of class C fly ash for aggregate production; (2) other efforts to produce synthetic aggregates, especially those using cementitious materials; (3) appropriate cut strand fibers and fiber fillers that may be used for ash-fiber-sand aggregate production; and (4) characterization methods for aggregates in various construction applications.

Fly Ash Aggregates: The main finding from the literature review is that little effort has been made to exploit the self-cementing property of ashes to produce aggregates. Most of the aggregate production methods using fly ash that are available in open literature involve some type of high temperature sintering (ACAA 1999). However, Baykal and Doven (1999) from Turkey have attempted to make unsintered fly ash aggregates using a combination of fly ash, Portland cement and lime. They have reported that Portland cement concrete made using this aggregate yielded 28-day strength in the range of 28 MPa to 35 MPa, which is similar to that of structural concrete. Bykal and Doven (1999) used ash that would classify as class F ash and they had to utilize Portland cement and lime as pozzolanic activators to produce the cementation within aggregates. This finding is encouraging and indicates that aggregates may be created without the expense of high temperature treatment. We note that the current research project envisages the exploitation of self-cementing capability of class C fly ashes to produce unsintered aggregates.

Baykal and Doven (2000) have presented further results on manufactured lightweight aggregates produced by pelletizing method using three mixes, 1) fly ash only, 2) fly ash and lime, and 3) fly ash and cement. The production rate and power consumption of the pelletization process depends on the physical properties of the agglomerated materials, the moisture content of the fines and the mechanical parameters. The fly ash used in this study has a specific gravity of 2.18 and a fineness of 24 μm. Based upon the chemical composition, this fly ash would be classified as class F fly ash. The pelletized aggregates were cured at 21°C and 70% humidity. The properties of the aggregates are summarized in the table below. The unit weight of the aggregates with fly ash only was found to be 9.6 kN/m^3. The aggregates formed with the addition of lime and cement had unit weights of 9.8 and 10.4 kN/m^3, respectively, which represent an increase of 2 to 8 %. The specific gravity for the aggregates varied from 2.00 to 2.35, and the absorption capacity varied from 28.8% to 33.9%. The optimum moisture content and maximum dry density from standard Proctor test were found to be 34-34.5% and 11.96-12.56 kN/m^3, respectively. The corresponding CBR values ranged from 58 to 82. The compaction test results show that the optimum moisture content is about 4-4.5 % more than the absorbed amount, which is similar to that for natural aggregates. The soundness test indicated that the loss of weight varies from 6.9% to 9%, which is well below the specified 12%. The finding of Baykal and Doven is encouraging as they indicate that cementitious capacity may be exploited to produce fly ash aggregates.

Properties		Fly ash	Fly ash and Lime	Fly-ash and cement
Unit Weight (kN/m^3)		9.6	9.8	10.4
Specific Gravity		2.00-2.17	2.10-2.28	2.17-2.35
Bulk Specific Gravity		1.19-1.29	1.26-1.33	1.33-1.40
CBR	Optimum Water Content (%)	34.4	34.5	34.0
	Dry Unit Weight (kN/m^3)	11.96	12.16	12.56
	CBR (%)	58	82	82
Soundness	9.5-4.75 mm size	9.0	8.9	7.4
	19-9.5 mm size	7.9	8.2	6.9
Absorption (%)		33.9-31.4	31.6-31.4	29.3-28.8

Along the lines of utilizing self-cementing capacity of class C fly ash, the work done by Kilgour et al. (1988) and Senadheera et al. (1998) has shown encouraging results. For example, ash pellets made in an agglomerator using class C fly ashes have been shown to have sufficient strength and durability for field handling and storage (Kilgour et al. 1988). In addition, compressive strengths as high as 15 MPa have been obtained for hydrated class C fly ash cured under controlled conditions (Senadheera et al. 1998). The samples were hydrated at three different moisture contents with no other additives or fillers, covered with polyethylene bags to prevent moisture loss, and cured at 70° F. Senadheera et al. reported that the aggregates obtained from fly ash hydrated at 20% moisture content had a specific gravity of 1.85 and satisfied the Wet Ball Mill test specification for Texas Department of Transportation Grade I flexible base materials.

Aggregates obtained from class C fly ashes hydrated in ash ponds have also been successfully used as road base material by the Texas Department of Transportation in experimental projects. These ponded ash aggregate road bases have a tendency to harden into a stiff layer after placement and compaction (Senadheera et al 1998). Similarly, visual inspections of the access road project at the KCPL Hawthorn site show that compacted ponded ash may be used to produce hard, cemented sub-grades. Therefore, it is reasonable to expect that hydrated ponded ashes have some residual cementing capacity, which may be enhanced by pozzolanic activators. Residual cementing capacity has also been observed by Bergeson and Mahrt (2000), who used reclaimed fly ash for fill under PCC pavement.

The paper by Bijen (1986) reviews the processes of manufacturing lightweight aggregates by using fly ash. According to this paper, the agglomeration process may be divide into two categories 1) Agitation granulation and 2) Compacting. The agitation granulation can be divided as disc granulation, drum granulation, cone granulation, and mixer granulation. The density of the pellets produced by compaction agglomeration is higher than that of pellets produced by agitation granulation. The resultant aggregate may be hardened by different processes 1) Sintering, 2) Hydrothermal process and 2) Cold Bonding. In hydrothermal process the bonding is achieved by means of chemical reaction of lime or Portland cement with fly ash and water. The hydrothermal process is more or less related to ore pelletizing. In Cold bonding the bonding is achieved by the reaction of fly ash with calcium hydroxide at ordinary temperature to form a weather-resisting bonding material. But the bonding of the material achieved by this method is less rigid than what is achieved by other method, this negative aspect can over come by using compaction agglomeration technique. This paper doesn't deal with the test result. Research is conducted to produce a light weight aggregates from a mixture of fly ash, wet desulphurization scrubber sludge and lime. The blocks are made from this composition and are crushed for the production of aggregates. Experiments have been performed to produce crushed aggregates from demolished artificial stone. Here they construct a base with mixture of fly ash, lime, gypsum and water and compacted. After hardening of this material it is crushed into an artificial aggregates.

Fibers in Cementitious Matrix: A variety of fibers have been used in cementitious composites (Balaguru and Shah 1992). In the proposed research project, the purpose of utilizing fibers is to provide the aggregates enhanced properties in terms of toughness, durability, crack resistance and impact strength, and reduced pre-existing shrinkage cracks. Glass, plastic and cellulose fibers have been generally used in cementitious products with varying degree of success. The fiber sizes used in these products vary from 2 mm to 30 mm. Based upon a literature review of fibers utilized with cementitious materials and considering the size of aggregates planned, we have selected three commercially available fibers: (1) milled glass fibers, (2) milled plastic fibers, (3) cellulose fibers. All the three chosen fibers have a size smaller than 1 mm. Of these, the milled plastic fibers are marketed primarily for application in cementitious materials as replacement for asbestos. The others are not marketed directly for cementitious material applications, however, have physical characteristics similar to the milled plastic fibers.

III. PHYSICAL AND CHEMICAL COMPOSITION OF KCPL CLASS C FLY ASH

Fly ash is obtained as a by-product from electricity generating utilities that use pulverized coal powder consisting of 70 to 80% particles passing No. 200 sieve (75 μm). The non-combustible elements in powdered coal evaporate at high temperatures and combine to form a variety of complex inorganic compounds. Upon the cooling of exhaust gases, these compounds precipitate into fine spherical particles. These particles may be collected using a variety of methods such as mechanical collectors, electrostatic precipitators, fabric bag filters and wet scrubbers. The fly ashes from the plants of Kansas City Power and Light Company (KCPL), which this paper focuses upon, are collected using electric precipitators. As part of the current project, a database of physical and chemical properties and their statistical variability has been compiled for the KCPL fly ash being utilized for making aggregate. The database serves as a point of comparison of this fly ash characteristics with other fly ashes reported in the literature. In addition, the database documents the variability of these fly ashes. In the following discussion, we briefly describe the physical and chemical characteristics of KCPL fly ashes. We also briefly discuss the following: (1) the differences between high-calcium fly ashes and low-calcium ashes, and (2) the statistical variability of fly ash properties.

Table 1 summarizes the mean and standard deviations of physical and chemical characteristics based upon data compiled for KCPL fly ashes. Table 1 also contains the data for fly ashes derived from Western or Powder River Basin coal based upon data available in the literature (Misra 1998). Literature data has been grouped into 3 classes based upon the calcium oxide (CaO) content of <10%, 10 to 20% and >20%. It is noteworthy that high calcium (class C) fly ashes, particularly the Western coal fly ashes, show small variability in almost all measures of physical and chemical characteristics. Similarly, the fly ashes obtained from KCPL, which are derived from Western coal combustion, also show a small variability. The low variability is attributable to the awareness of the power plants to control the quality of their combustion by-product as well as the low natural variability of the Western coal. It is also noteworthy that the class C fly ash used in this project has low loss-on-ignition and fineness values, which makes it an excellent cement surrogate.

Particle Morphology, Grain Sizes, Specific Gravity and Bulk Density: In the proposed project we are utilizing class C fly ash obtained from KCPL Iatan plant. This fly ash appears as a fine powdery material with mainly spherical glassy particles, consisting of solid spheres; glass bubbles termed cenospheres; and cenospheres that are packed with smaller spheres termed plerospheres. A small amount of irregular shaped particles are also present that consist of mainly crystalline materials. For fly ashes, the grain sizes are typically specified in terms of: (i) fineness, (ii) specific surface, and (iii) cumulative grain size distribution curves. ASTM C618 specifies the fineness in terms of amount retained on No. 325 (45 μm) sieve, which should be no more than 34% by weight. Figure 1 gives a range grain size distributions observed for various fly ashes. The fineness of KCPL fly ashes is shown by the filled symbol.

Table 1 lists the typical specific gravity values for a variety of fly ashes along with the KCPL fly ashes considered in this project. A review of the literature indicates that the bulk density of different fly ashes also varies over a large range, from 0.5 to 0.9 g/cm^3. The bulk density variations reflect the compaction conditions. The bulk densities of lightly compacted KCPL fly ashes have been measured to vary between 0.75 to 0.8 g/cm^3.

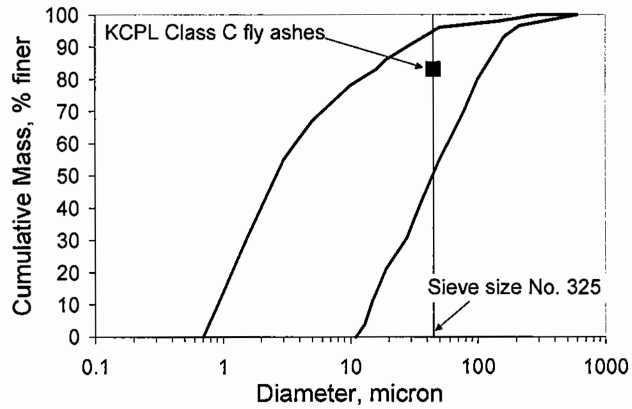


Figure 1. Grain size distribution for fly ashes.

Strength Gain Characteristics and Hydration Moisture Requirements: Tests were conducted on LaCygne class C fly ash to find the strength gain characteristics and hydration moisture requirements of class C fly ash. These tests were conducted according to ASTM D5239. Figure 2 shows the relationship between strength gain and curing age, and hydration moisture requirements and curing age. As shown the strength of the fly ash increases as the curing age increase. The rate of strength gain is the highest in the first 7 days. The rate considerably slows down the next 7-days; and there is little strength gain between 7 to 14 days. Beyond 14-days, the strength gain is negligible. Thus, it maybe concluded that most of the hydration reaction in fly ash takes place between 1 to 14 days. A second set of test was conducted by modifying the water-fly ash ratio to be 0.3 as opposed to 0.35 used in the ASTM D5239. As shown in Figure 2, the strengths are generally higher for water-fly ash ratio of 0.3. We also studied the moisture loss during curing. Results show that 13 percent to 17 percent of moisture is needed by fly ash for hydration.

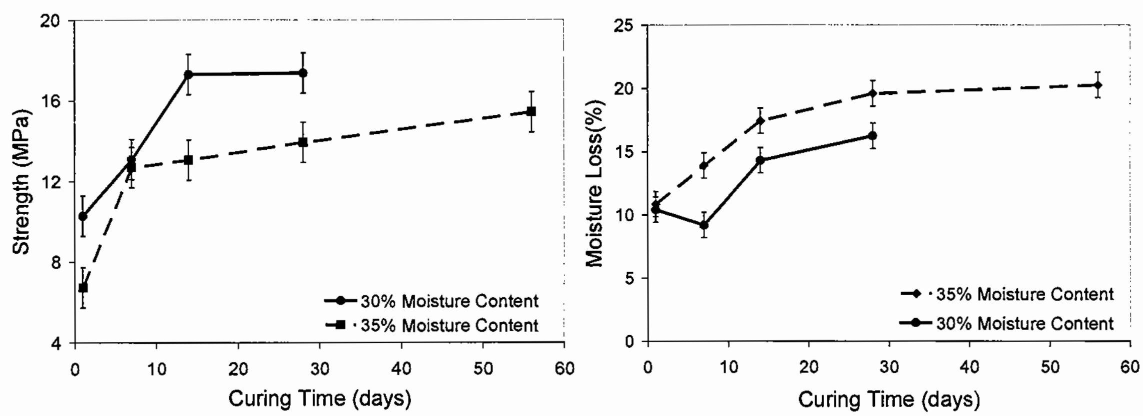


Figure 2. Plot of strength gain and hydration moisture with curing days.

Chemical Composition: Class C fly ash is mainly composed of silicon, aluminum, and calcium oxides as well as complex combinations of these oxides. In addition small amounts of iron and magnesium oxides, active alkalis, such as sodium and potassium oxides, and unburned carbon are also present. Table 1 summarizes the chemical composition of various fly ashes. Considering calcium oxide content, fly ashes are categorized as: (1) low (<10% CaO), (2) medium (10-20% CaO), and (3) high (>20% CaO) calcium fly ash. Furthermore, depending upon the relative amounts of the major chemical constituents, fly ash may be classified as Class C and Class F. Fly ash containing more than 50% but less than 70% of silicon, aluminum and iron oxides (SiO_2+Al_2O_3+Fe_2O_3) are classified as Class C. If the sum of these three oxides exceeds 70% then a fly ash is classified as Class F. Thus the medium and high calcium fly ash are considered as Class C fly ash. As seen from Table 1, the combustion of Western coal (a sub-bituminous coal) typically produces a Class C fly ash. Class C fly ash, such as those obtained from KCPL's Hawthorn, LaCygne and Iatan plants; contain sufficient calcium and other compounds to induce a cementitious reaction in the presence of water, which makes these fly ashes applicable as a cementing agent. As seen from the ternary diagram in Figure 3, which gives the oxide composition of fly ashes along with those of Portland cement, natural cement and quick lime, the KCPL fly ashes have chemical characteristics that are close to natural hydraulic cements.

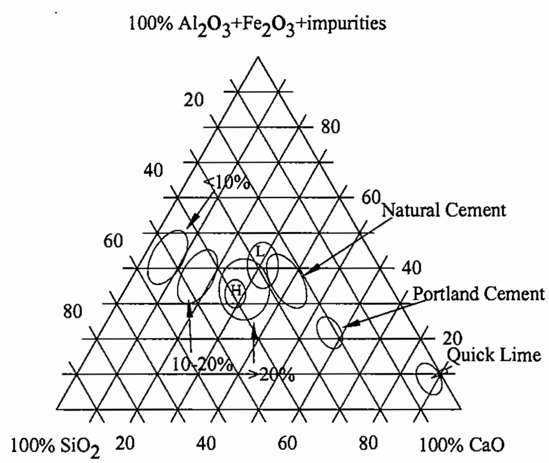


Figure 3. Ternary diagram of oxide composition of fly ashes.

Table 1. Physical and Chemical Characteristics of Fly Ash

Component	Class F fly ash*		Class C fly ash*				Typical Western* coal ash (estimated)		Hawthorn [a] ash		LaCygne [b] ash		Iatan [c] ash	
	< 10 % CaO		10-20 % CaO		>20 % CaO									
	M[d]	D[e]	M	D	M	D	M	D	M	D	M	D	M	D
MC	0.11	0.14	0.1	0.0	0.06	0.06	0.059	0.005	0.091	0.018	0.076	0.025	0.05	0.02
LOI	2.6	2.4	0.5	0.7	0.33	0.05	0.37	0.108	0.316	0.104	0.341	0.147	0.44	1.91
Fineness	23	9	20	7	15	4.9	14	3.4	15.82	1.057	12.28	1.540	20.8	1.99
Specific Gravity	2.19	0.36	2.4	0.14	2.61	0.10	2.6	0.05	2.598	0.027	2.571	0.033	2.52	0.05
SiO_2	52.2	9.6	48.5	4.8	36.9	4.7	35.1	1.52	34.29	2.46	34.09	2.13	41.16	1.76
Al_2O_3	22.8	5.4	19.6	3.6	17.6	2.7	17.6	0.45	23.23	0.75	22.67	0.98	22.28	0.87
Fe_2O_3	7.5	4.3	6.2	2.1	6.2	1.1	5.8	0.35	5.41	0.30	5.86	0.41	5.28	0.33
Sum	82.8	13.1	74.3	4.4	60.7	5.2	58.5	1.62	62.92	2.06	61.67	1.78	68.76	1.53
SO_3	0.6	0.5	1.3	0.8	2.9	1.8	3.1	0.45	1.46	0.20	1.70	0.20	0.93	0.18
CaO	4.9	2.9	15.2	2.5	25.2	2.8	25.9	0.79	25.13	1.29	26.70	1.36	21.99	1.10
AA	0.8	0.9	1.0	0.9	5.1	1.0	2.2	0.45	1.40	0.06	1.38	0.05	1.09	0.10
MgO	-	-	-	-	-	-	-	-	-	-	-	-	4.09	0.27

[a]-------based upon 13 samples collected between February 1996 and June 1996. [b]-------based upon 18 samples collected between February 1996 and June 1996. [c]-------based upon 98 samples collected between January 2001 and May 2001. *-------data from McCarthy et al. 1989[1]. [d]---------Mean. [e]---------Std. Deviation. MC---moisture content. LOI---loss on ignition. Sum---SiO_2+Al_2O_3+Fe_2O_3. AA---available alkalis.

IV. CLASS C FLY ASH AGGREGATES

Class C Fly Ash-Fiber-Sand Mortar

To evaluate the application of class C fly ash as hydraulic cement for making low to intermediate strength material, fly ash-sand mortar mixtures were investigated. Mortar mixes were made for water-fly ash ratios of 0.2, 0.3 and 0.4 and for sand-fly ash ratios of 1.5, 2.0 and 2.5. To ensure uniformity in mix and cube preparation, the mortar was thoroughly mixed in a motorized mixer for exactly 5 minutes and then placed in a mold in three layers with each layer compacted 25-times using a tamper. Three cubes were prepared for each mix proportion and air cured for 7-days at 74±3 °F (23±1.7 °C). The cubes yielded very consistent strength results, therefore, three cubes per mixture were deemed to be acceptable for determination of optimum mix proportion. Figure 4 shows the contour plot of 7-day compressive strengths. The optimum mortar mix was found to have the water-fly ash-sand proportion of 0.3:1.0:2.0 with strength in excess of 10MPa.

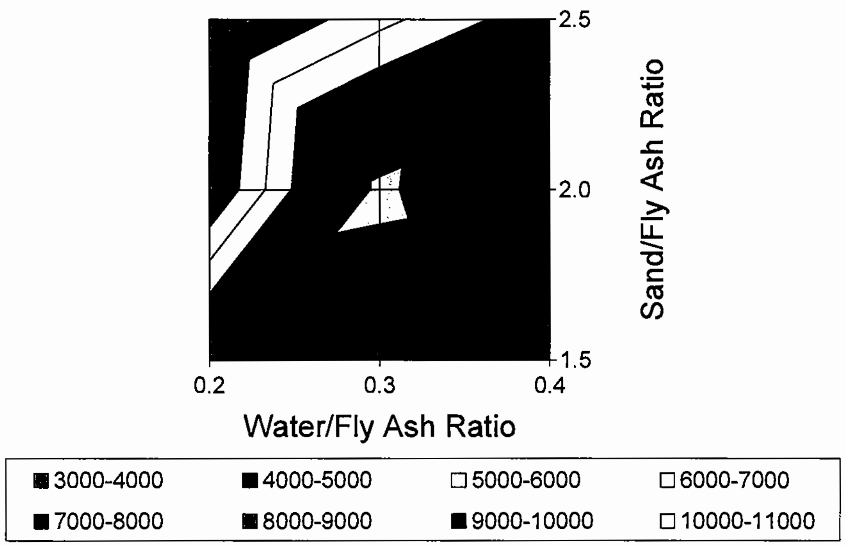


Figure 4. Contour plot of 7-day compressive strengths in kPa.

To further explore the variability of mechanical behavior of fly ash-sand mortar, 21 additional cubes were prepared and cured for 7-days in an environmental chamber at 90% humidity and 95°F (35°C) temperature. Figure 5 gives the histogram of the compressive strength and modulus of elasticity for the mix proportion 0.3:1.0:2.0. The mean and standard deviation of compressive strength was found to be 14.6 MPa and 1.23 MPa, while that for modulus of elasticity was found to be 710 MPa and 60 MPa, respectively. Notably, the coefficient of variation, determined as a ratio of the standard deviation and the mean, is less than 10% indicating low variability in strength and modulus of elasticity.

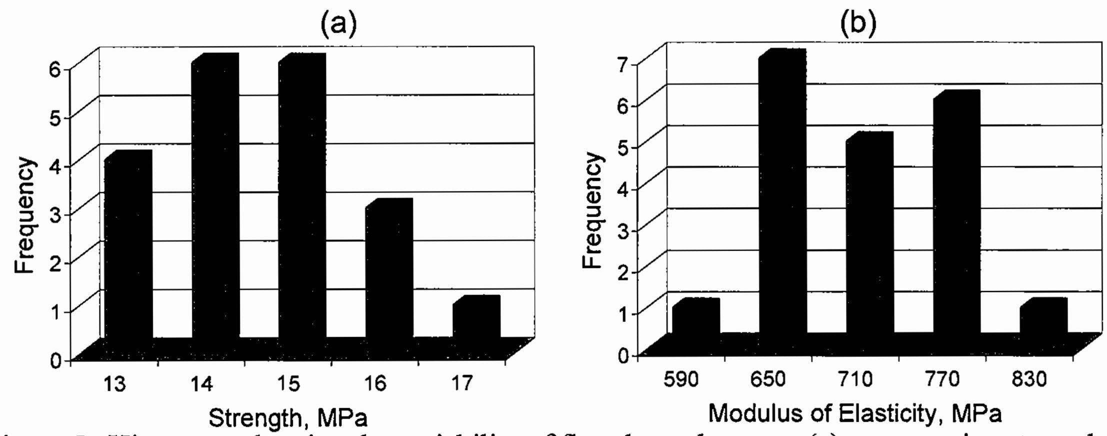


Figure 5. Histogram showing the variability of fly ash-sand mortar, (a) compressive strength, and (b) modulus of elasticity, after 7-day curing.

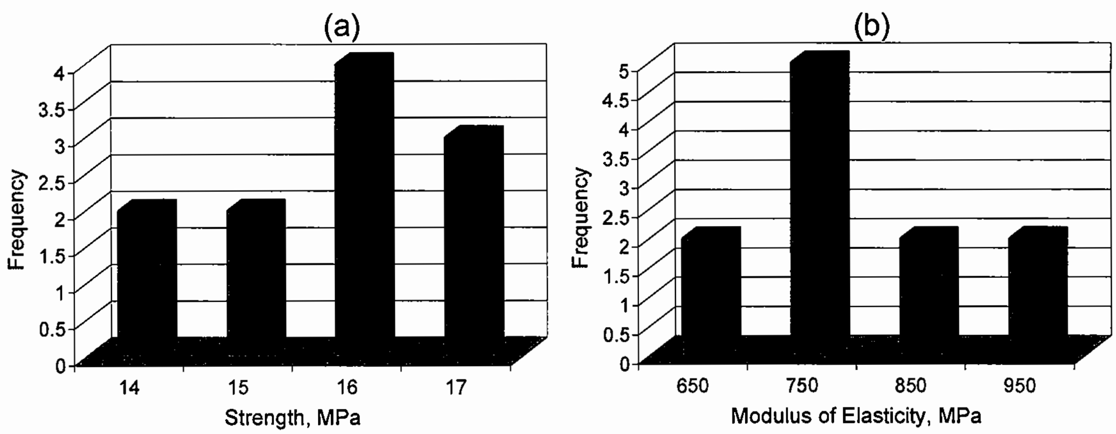


Figure 6. Histogram showing the variability of fly ash-sand mortar, (a) compressive strength, and (b) modulus of elasticity, after 14-day curing.

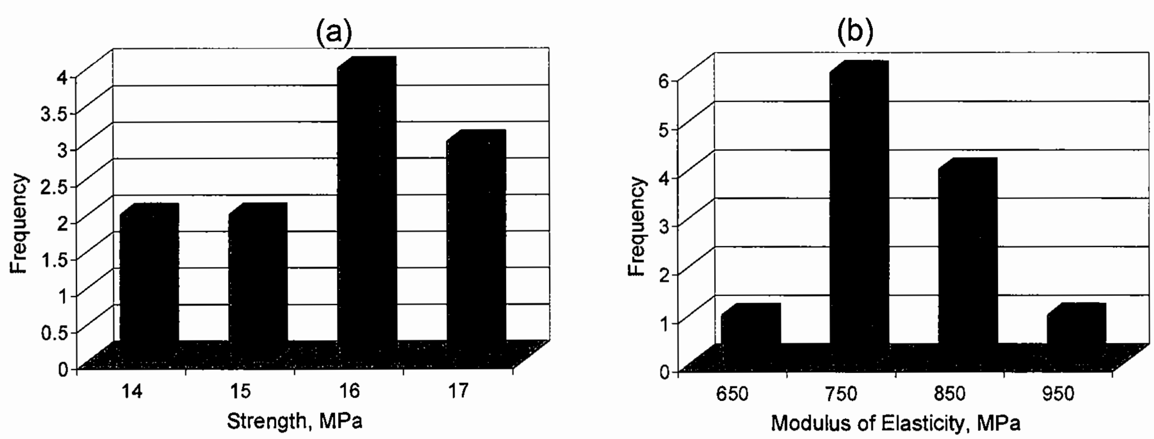


Figure 7. Histogram showing the variability of fly ash-sand mortar, (a) compressive strength, and (b) modulus of elasticity, after 28-day curing.

Furthermore to verify that the 7-day strength is representative of the fly ash-sand mortar behavior, two batches of 21 additional cubes were prepared and cured in an environmental chamber at 90% humidity and 95°F (35°C) temperature and tested for 14 and 28-day strengths. Figures 6 and 7 give the histogram of the compressive strength and modulus of elasticity for 14-day and 28-day cured samples, respectively. As seen from the histograms and Figure 8, the 14-day and 28-day average compressive strength and modulus of elasticity are very close. Clearly a majority of the strength gain occurs within the first 7-days of curing.

Class C fly ash was found to have rapid initial hydration rate and a short set time. Vicat penetration apparatus was utilized to explore the initial hydration rate of fly ash-sand mortar. Since the initial hydration rate is rapid, the needle penetration is recorded every 45 seconds until the needle is unable to penetrate the mortar. This is in sharp contrast to the standard Vicat penetration test used for Portland cement, wherein the penetration is recorded every 30 minutes. Figure 9a gives a record of penetration versus time curve for the optimal fly ash-sand mortar. Again three mortar samples were tested to confirm the repeatability of the penetration tests. An average set time of 12 minutes was recorded for this mortar.

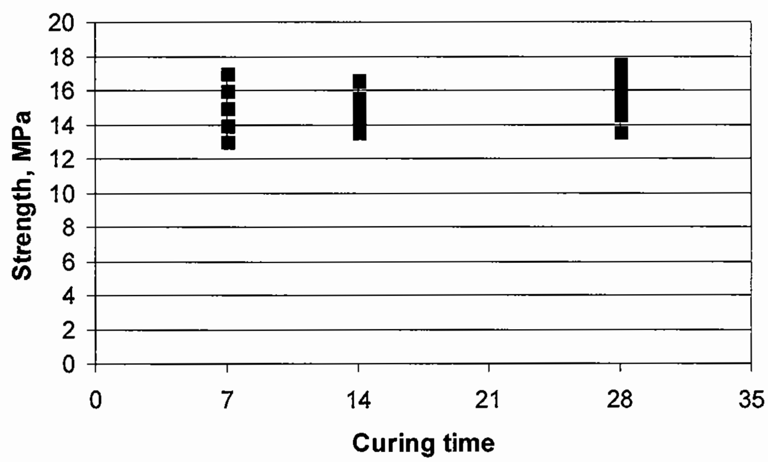


Figure 8. Strength of fly ash-sand mortar versus the time of curing

With the view that the rapid hydration time could be of concern in some application, we evaluated a commercially available retardant used for Portland cements. The retardant was effective in increasing the setting time for the mortars. Figure 8b gives the penetration curve for fly ash-sand mortar prepared with retardant. The retardant used in these tests is marketed for use with Portland cements; therefore the effect of dosage rate on setting time and compressive strength of fly ash-sand mortar was investigated. Figure 10 gives a plot of setting time and compressive strength versus the retardant dosage rate. The retardant has a small effect on compressive strength up to a dosage rate of 150ml/ 100kg of fly ash, while the setting time is increased by almost 50%. At higher dosage rates, the strength falls rapidly and the setting time increases rapidly as well. As a dosage rate of 250ml/ 100kg of fly ash, the strength is decreased by almost 25% to 7.8 MPa, while the setting time is increased by 200% to 36 minutes.

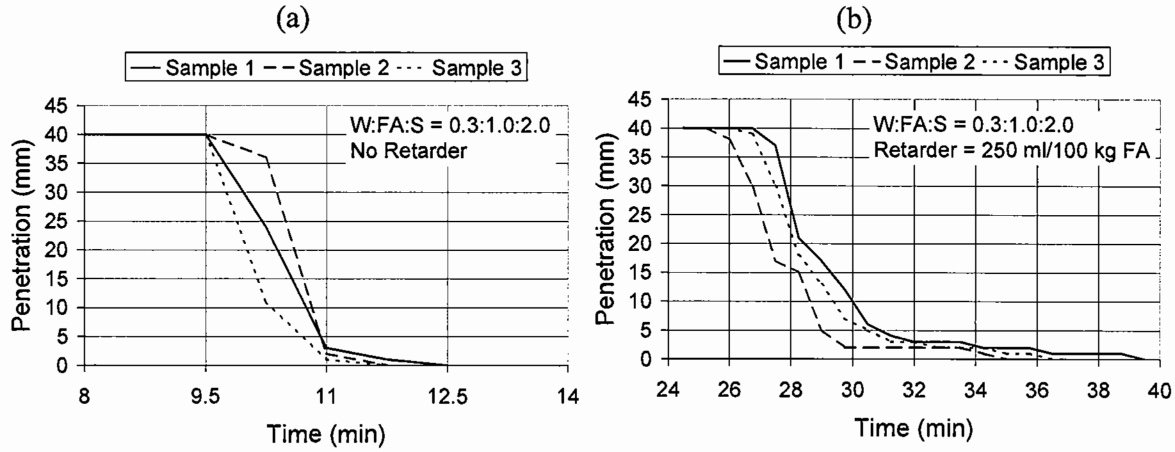


Figure 9. Penetration curve for fly ash-sand mortar.

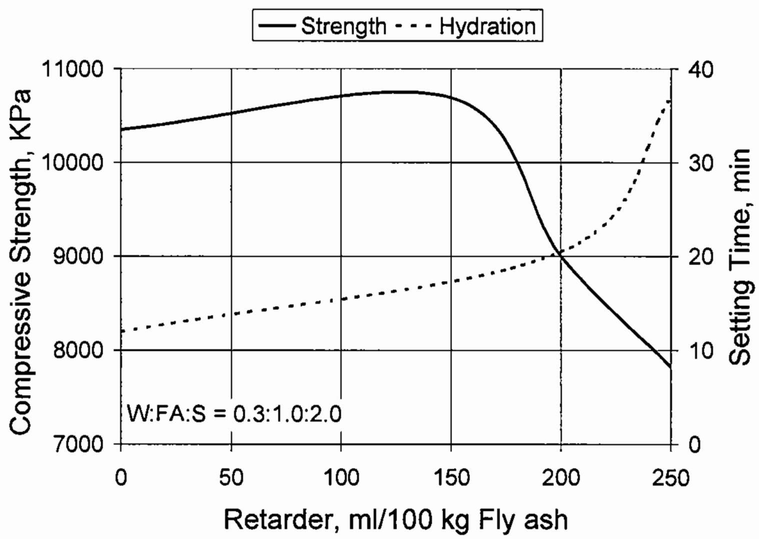


Figure 10. Effect of retardant of fly ash-sand mortar behavior

Class C Fly Ash-Fiber-Sand Mortar

Based upon the above tests, the water-fly ash-sand proportion of 0.3:1.0:2.0 is deemed to be optimal. Further testing is now underway to determine the optimal contents of the three fibers chosen for evaluation. Figures 11 through 16 give the histogram of the compressive strength and modulus of elasticity for mortars prepared by replacing sand with fibers. Glass fibers were used to replace sand at three replacement levels of 5%, 10% and 15%, while polymer fibers were used at the replacement levels of 5% and 10%, and cellulose fibers at the replacement level of 10%.

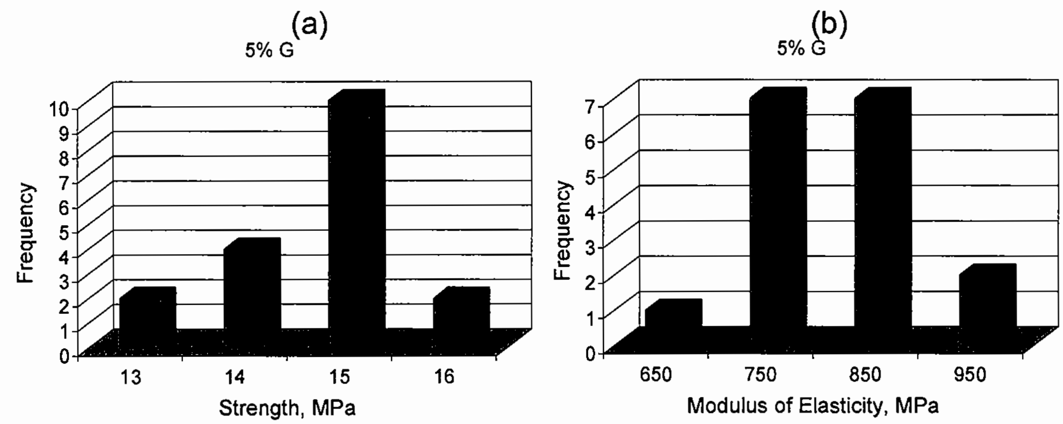


Figure 11. Histogram showing the variability of, (a) compressive strength, and (b) modulus of elasticity for fly ash-fiber-sand mortar containing 5% glass fibers.

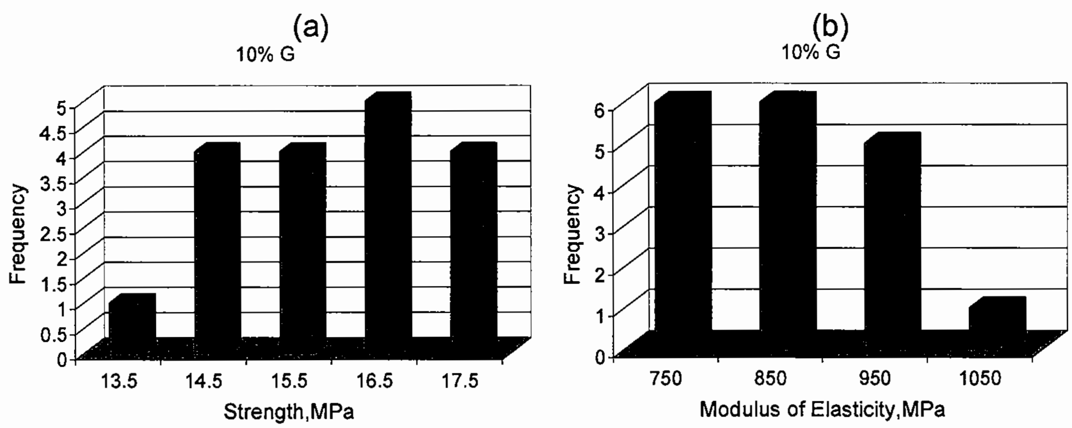


Figure 12. Histogram showing the variability of, (a) compressive strength, and (b) modulus of elasticity for fly ash-fiber-sand mortar containing 10% glass fibers.

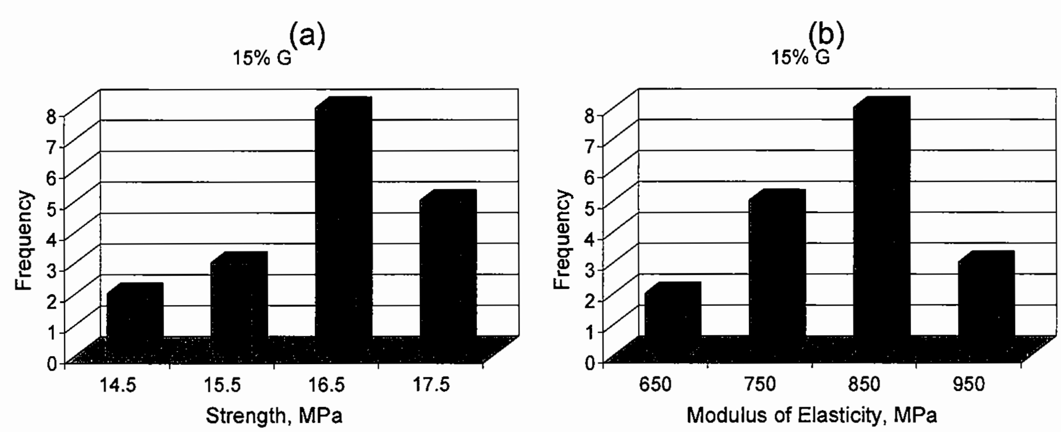


Figure 13. Histogram showing the variability of, (a) compressive strength, and (b) modulus of elasticity for fly ash-fiber-sand mortar containing 15% glass fibers.

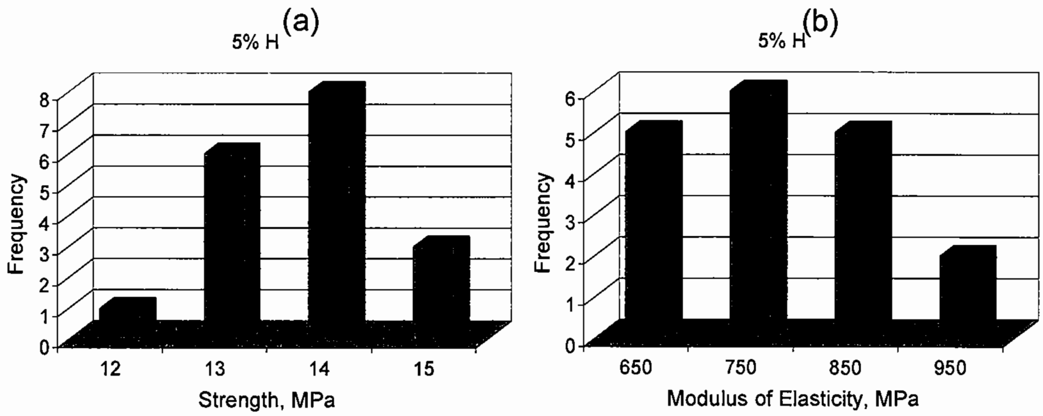


Figure 14. Histogram showing the variability of, (a) compressive strength, and (b) modulus of elasticity for fly ash-fiber-sand mortar containing 5% polymer fibers.

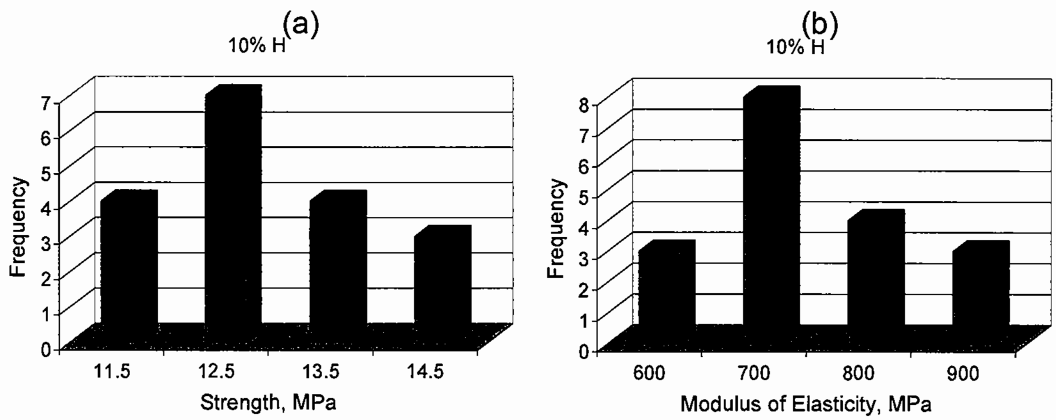


Figure 15. Histogram showing the variability of, (a) compressive strength, and (b) modulus of elasticity for fly ash-fiber-sand mortar containing 10% polymer fibers.

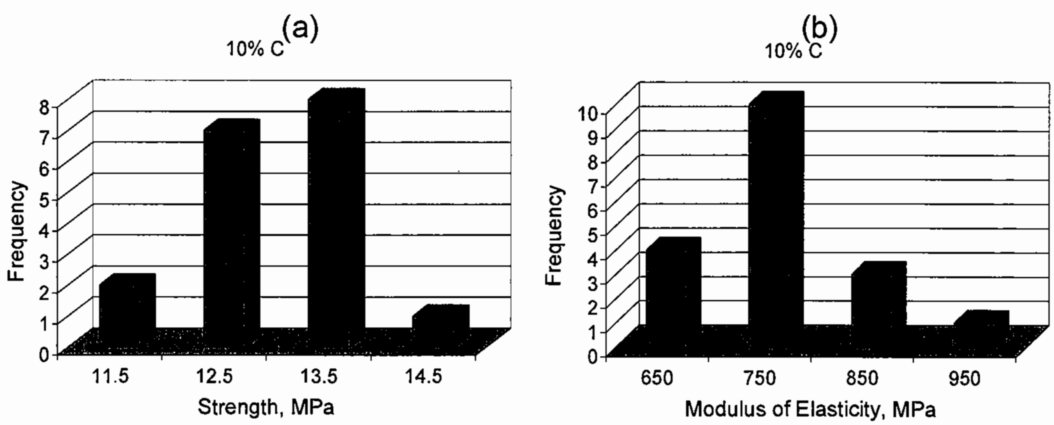


Figure 16. Histogram showing the variability of, (a) compressive strength, and (b) modulus of elasticity for fly ash-fiber-sand mortar containing 10% cellulose fibers.

The histograms in Figures 11 through 16 are based upon tests conducted on 18-cubes for each mix cured for 7-days in an environmental chamber at 90% humidity and 95°F (35°C) temperature. The average and standard deviations of strength and modulus of elasticity are tabulated in Tables 2 and 3. Fairly repeatable results are obtained in all cases. Remarkably, the standard deviations for the strength are in the range of 5% to 8%, indicating repeatability of mix and cube preparation. As seen from Tables 2 and 3, the glass fiber increases both the strength and modulus of elasticity of fly ash-sand mixtures. In contrast, the plastic and cellulose fibers tend to decrease the strength while increasing the modulus of elasticity. Although the change in compressive strengths and modulus of elasticity due to addition of fibers may appear to be low, the durability and toughness are expected to increase considerably. As outlined in the original proposal, we intend to perform toughness and durability tests on the final aggregates produced using these mixes to quantify the toughness and durability parameters.

Table 2. Compressive strength of fly ash-fiber-sand mortar, MPa

% Fiber by volume	Glass Fiber		Hi-Fibe (plastic)		Cellulose Fiber	
	Range	Average (Standard Deviation)	Range	Average (Standard Deviation)	Range	Average (Standard Deviation)
5	13.62-16.34	15.21 (0.75)	11.77-15.45	13.78 (0.84)		
10	12.53-17.65	15.76 (1.32)	11.46-14.79	12.72 (0.95)	11.10-14.27	12.89 (0.74)
15	14.76-17.29	16.37 (0.88)				
50	8.69-10.34	9.55 (0.71)				

Table 3. Modulus of elasticity fly ash-fiber-sand mortar, MPa

% Fiber by volume	Glass Fiber		Hi-Fibe (plastic)		Cellulose Fiber	
	Range	Average (Standard Deviation)	Range	Average (Standard Deviation)	Range	Average (Standard Deviation)
5	686-1002	822 (79.2)	611-933	770 (99.6)		
10	712-1121	855 (105.8)	663-924	740 (96.0)	662-988	749 (79.2)
15	618-944	816 (89.5)				

To further explore the effect of the retardant on behavior of fly ash-fiber-sand mortar, we prepared 5 cubes adding 5% gypsum and additional 6 cubes with 2% gypsum. We cured the cubes for 7-days in an environmental chamber at 90% humidity and 95°F (35°C) temperature. The retardant was a pure white, smooth, slow-setting plaster. The mortar was prepared by replacing fly ash with calcium sulfate and the cubes were prepared in the manner described earlier. The strength and modulus of elasticity of the resulting mortar are given in Table 4.

As seen from Figure 17, the average strength for the mortars with 2% and 5% gypsum are similar - 11.905 MPa and 12.72 MPa, respectively. Therefore additional test was performed to determine which mixture has the better workability. For this purpose, we prepared three fly ash-water samples with 0%, 2% and 5% calcium sulfate. The setting time for the mixtures with 2% and 5% increased. Given that the difference between the setting times of the 2% and 5% were not immense, but the workability for the 2% gypsum improved, we chose the 2% gypsum to be the better amount for aggregate production.

Table 4. Strength and Modulus of Elasticity for mortars with 2% and 5% calcium sulfate.

% Gypsum by volume	15 % Glass Fiber				50 % Glass Fiber			
	Compressive Strength, MPa		Modulus of Elasticity, MPa		Compressive Strength, MPa		Modulus of Elasticity, MPa	
	Range	Average (Stdev)	Range	Average (Stdev)	Range	Average (Stdev)	Range	Average (Stdev)
2 %	11.09-12.41	11.905 (0.49)	579-769	671 (64.2)	8.69-10.34	9.55 (0.71)	391-595	517 (80.8)
5 %	11.38-13.62	12.72 (0.84)	470-918	626 (184)				

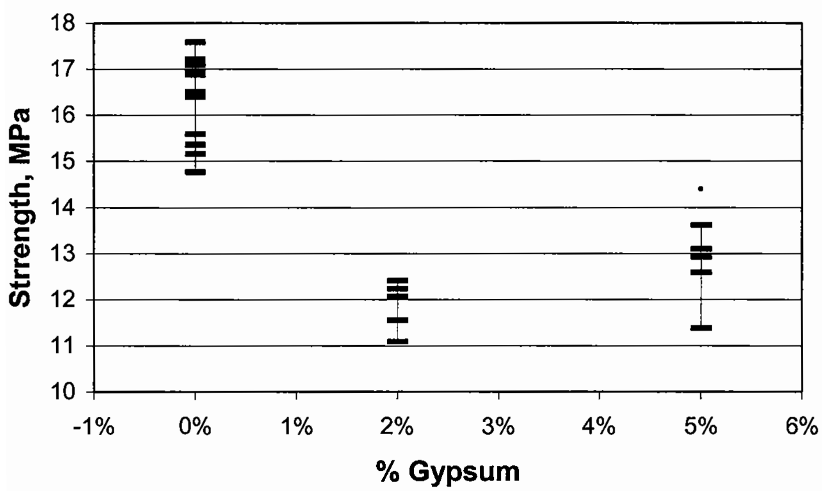


Figure 17. Strength of the samples for 0%, 2% and 5% gypsum

Class C Fly Ash-Fiber-Sand Aggregates:

Extruded Aggregates:

Based upon the results of Task 2 described above, we have determined the optimal mix proportion of water-fly ash-sand proportion to be 0.3:1.0:2.0. Based upon strength consideration, the most effective fiber type identified to be glass fibers at the replacement rates of 15% by volume of sand. However, based upon workability considerations, glass fibers at the replacement rates of 50% by volume of sand were found to be effective. Using these mix-proportions and fiber type and content, aggregate samples were produced utilizing an extrusion process.

The preparation of the extruded mixtures was as follows: first the solid materials (fly ash and fine sand passing # 40 sieve, 0.425 mm) were mixed together with the fibers to get proper dispersion of the fibers in the composite, and then water was incorporated to the mixture. All the components were mixed together manually, since the batches were too small for the mixer. The mixture is subsequently extruded through a die. The extruded aggregates are cured under plastic sheet cover in an environmental chamber at 90% humidity and 95°F (35°C) temperature. After one day the plastic wrapping is removed and the aggregates are cured in the environmental chamber at the same humidity and temperature for 6 days. Another batch of aggregates was cured under plastic cover at room temperature (23 °C) and 70% humidity. After one day, these aggregates were placed in water to cure at 100 % humidity for at least 6 days. Thereafter the specimens were dried at 70% humidity and room temperature (23 °C) for 24 hours for aggregate property determination.

A variety of laboratory tests were performed to characterize the properties of the resulting extruded aggregates. We narrowed the number of selected mix proportions to two. Density, specific gravity and absorption capacity tests were conducted on two mix proportions:

- 15 % glass fiber, water-fly ash-sand = 0.3: 1.0: 2.0
- 50% glass fiber, water-fly ash-sand = 0.33-1.0-0.33, 2% gypsum.

The remaining tests were performed on aggregates with 50 % glass fiber, water-fly ash-sand ratio 0.33-1.0-0.33 and 2% gypsum. These tests were performed several times to make the test results statistically meaningful.

Particle shape and surface texture tests were conducted to measure particle angularity and flakiness. These properties are particularly important in the utilization of aggregates as road base course materials. Generally, angular aggregates produce bulk materials with higher stability than rounded aggregates. However, the angular aggregates are more difficult to work into place than rounded aggregates, since its shape makes it difficult for them to slide across each other. The produced crushed aggregates have a rounded shape. Furthermore, surface texture is also an important property that controls the compaction behavior and the shear strength of the bulk material. As such, these properties are important indicators of the aggregate performance. The extruded aggregates have a rough surface, which is desirable for base courses in order to increase the stability of the materials in the field.

Gradation test was performed to document the grain size distribution of the crushed aggregates. The gradation test shows a one-sized distribution. One hundred percent of the aggregate amount retained on 12.5 mm sieve. One-sized graded aggregates have good permeability, but poor stability and could be used for chip seals of pavement.

Moisture absorption capacity, specific gravity and density tests were performed to measure the weight-volume characteristics of the aggregates. The density of the aggregates was determined according to ASTM D 1556. The specific gravity tests and the absorption test were conducted according to ASTM C127. Prior to the test, the aggregates were immersed in water at room temperature for 24 hours. Afterwards the aggregates were removed from the water and rolled in a towel until all visible films of water were removed. The test sample in saturated-surface dry condition were weighted and recorded. Following, the aggregates were placed in a wire basket and the weight was determined while it was submerged in water at a temperature of 23 °C. Finally the test sample was dried to a constant temperature of 110 °C and weighted. Table 10 shows the density, bulk specific gravity and apparent specific gravity as well as the absorption capacity of the tested aggregates. We can see how the results vary for the different mortar ratios, besides the bulk specific gravity.

Table 5. Extruded fly ash-sand-fiber aggregate properties.

Aggregate	Density [g/cm^3]	Bulk spec. Gravity (SSD)	Apparent spec. Gravity	Bulk spec. Gravity	Absorption [%]
15 % glass fiber, water-fly ash-sand = 0.3: 1.0: 2.0	1.163	3.37	3.64	1.78	90.5
50% glass fiber, water-fly ash-sand = 0.33-1.0-0.33, 2% gypsum	0.95	1.34	1.59	1.78	18

Soundness and durability tests were performed to determine the weathering resistance of the aggregates. We performed both, the sulfate resistance test (ASTM C88) and the freeze-thaw test (AASHTO T103) to determine the soundness of the fly ash-fiber-sand aggregates. The sulfate resistance test was performed according to ASTM C88 by using sodium sulfate. The samples were immersed in the prepared solution of sodium sulfate for not less than 16 h, nor more than 18 h. After the immersion period, the aggregate samples were removed from the solution and placed in the drying oven at 230 °F (110 °C). After constant weight has been achieved, the samples were cooled to room temperature and afterwards they were again immersed in the prepared solution. The process of alternate immersion and drying was repeated until 5 cycles were obtained. After completion of the required numbers of immersion and drying cycles, the sulfate salt was washed out of the sample and the aggregate sample was dried. The sample then was sieved trough 8 mm sieve, which is smaller than the original sieve (12.5 mm) on which the size fraction was retained. The resulting weighted average loss for the size fraction is used as indication of durability of the aggregate. The weight loss was found to be 89.8% indicating that these aggregates are especially susceptible to sulfate attack. The freeze-thaw test also resulted in large weight loss of 91.3%.

Crushed Aggregates:

After performing extensive laboratory test on extruded aggregates, we found that the material lost during soundness and durability test is excessive, absorption capacity is very high in some cases, and the abrasion resistance is low. Consequently, we decided to make crushed lightweight aggregates and perform laboratory test to find the weight –volume characteristics and engineering properties of these aggregates. We have produced crushed aggregates with three different methods. The two most critical aspects of crushed aggregate production are (1) curing of aggregates, and (2) crushing of aggregates to get dense-graded aggregates.

Three methods of crushed aggregate production have been investigated:

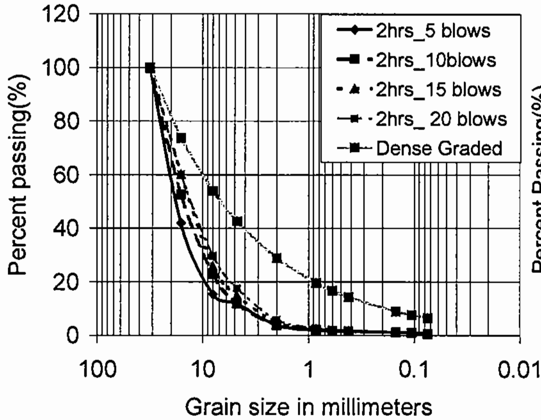
Procedure 1) Fly ash was mixed with 20 % moisture content by weight in a mixer for 2 to 3 minutes. The mix was then placed in a circular mold of size 3.0 inch in diameter and 1.5 inch in height and compacted at 1000 psi for 1-minute. Subsequently, a seating pressure of 600 psi was applied on the sample for 10 minutes to achieve proper compaction and to ensure that there is minimal rebound upon removal of seating pressure. The sample is then wrapped in plastic and aluminum foil and cured at 38°C and 75% humidity for 7 days. Thereafter the specimens were dried at room temperature (23°C) for 24 hours and crushed with 20 blows by 2.5 kg rammer.

Procedure 2) The samples were molded and cured using the method described in procedure 1. Subsequent to curing, the specimen was dried for a day at room temperature and then fired in a furnace at a temperature of 850°C for 2 hrs to bake. The sample was the crushed by the same method discussed in procedure 1.

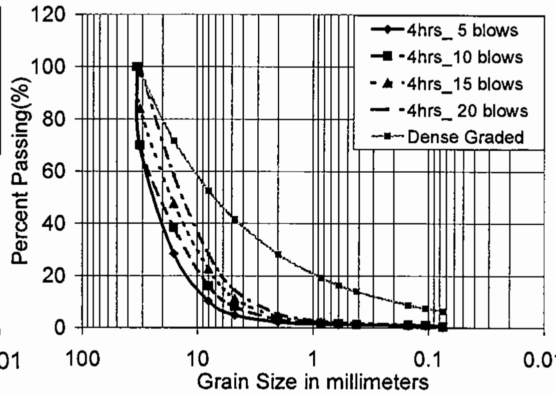
Procedure 3) The samples were molded and cured using the method described in procedure 1. Subsequent to curing, the specimen was dried for a day at room temperature and then fired in a furnace at a temperature of 850°C for 4 hrs to bake. The sample was the crushed by the same method discussed in procedure 1.

The size and weight of the samples were measured after the samples were demolded prior to curing. The compacted sample had a size 3.0 inch diameter and 1.47 inch height. The unit weight of the compacted samples came out to be 124 pcf. Samples were also weighed after they were cured and baked. It was seen that approximately 60 grams weight was lost during the baking process and the resultant unit weight of the sample was 102 pcf.

Figure 18a and 18b below shows the gradation of aggregates of 2 hrs and 4 hrs-baked samples, with different number of blows. It is seen that both the samples have approximately same percentage of fines passing through 2 mm sieve. Figure 19 below shows the comparison of gradation of aggregates made by 3 different methods with 20 blows.



(a)



(b)

Figure 18. Grain size distribution of crushed aggregates crushed at different input energy.

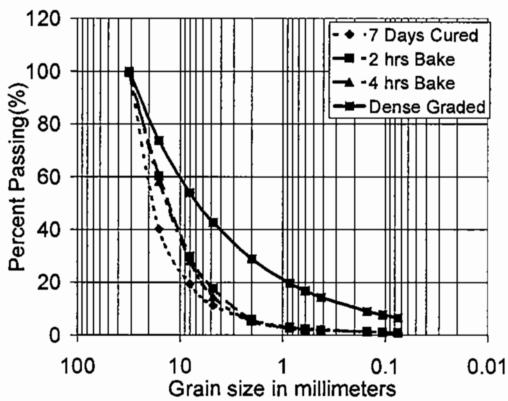
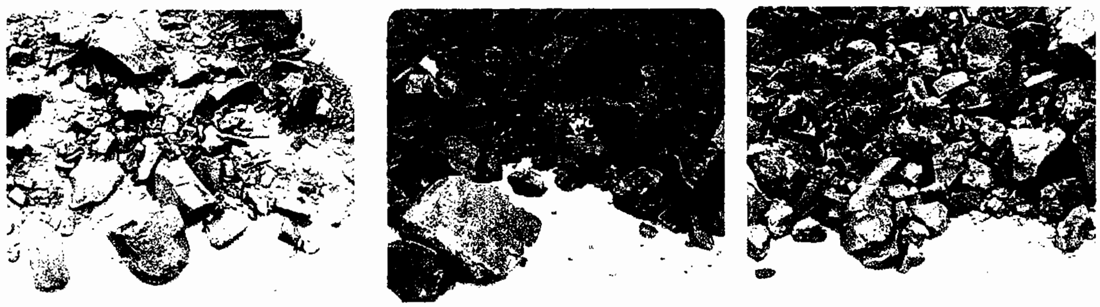


Figure 19. Comparison of grain size distribution of crushed aggregates.

Figure 20 shows the picture of 3 different samples made by different methods after 20 blows of 2.5 kg rammer. After examining the grain size distribution of different kinds of aggregates made with the above procedures, we have concluded that the aggregates made using procedure 1 have an applicable grain size distribution. Moreover, procedure 1 is expected to be more economical compared to the other two procedures, which require sintering at 850 °C. Therefore, the less energy intensive procedure 1 was further investigated for aggregate production. The aggregate properties were characterized with a view of grading these aggregates for quality and application.



Method 1 Method 2 Method 3

Figure 20. Pictures of crushed aggregates after 20 blows.

Specific Gravity, Bulk Density and Absorption Capacity

The crushed aggregates obtained from procedure 1 were used to determine the specific gravity, bulk density and absorption capacity. Specific gravity is the characteristic generally used for calculating the volume occupied by the aggregates in various mixtures that are proportioned or analyzed on an absolute volume basis. The test conducted on the lab-crushed aggregate was according to ASTM C127 standards. The specific gravity of material ranges between 1.73-1.75. The bulk density test on the lightweight aggregate was done according to ASTM C29 standards. The compact bulk density was determined by the rodding procedure during our laboratory test. The bulk density of aggregates ranges from 1.31 Mg/m^3 – 1.46 Mg/m^3. Absorption Capacity test was conducted according to ASTM C127. It was found that fly ash aggregate made by procedure 1 has an absorption capacity of 20%-22 %.

Index of Aggregate particle shape and texture

This test was conducted in accordance with (ASTM D 3398-00). To determine the particle index of aggregate we used sample, which passed through 9.5 mm sieve and retained on 4.75mm sieve due to short of sample. We selected this fraction of sample because from the grain size distribution curve we can see that our bulk sample have nearly have 40-50% of aggregates size which comes under this range. Void ratio for this fraction at 10 blows per layer was 35% and for 50 blows per layer was 29%. Particle index for this fraction of aggregate was 4.6.

Dry density and Moisture content relationship

The moisture-density relationship of the fly ash aggregates was determined according to ASTM D 1556. Figure 21 shows dry density and misture content relationship for light weight aggregates. The maximum dry density obtained was 1.61 Mg/m^3, at the optimum moisture content of 19%

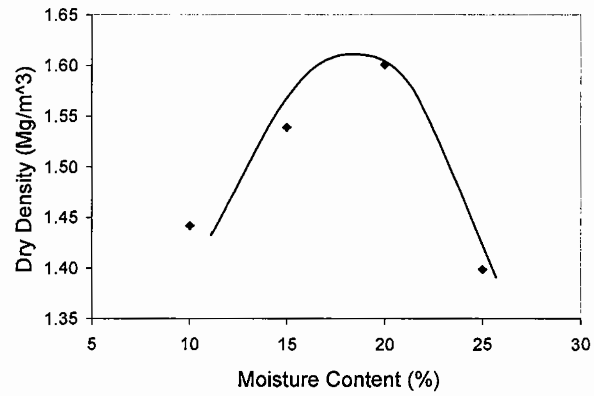


Figure 21: Compaction curves for aggregates.

California Bearing Ratio (CBR)

The California Bearing ratio (CBR) test (ASTM D1883) was performed on samples compacted in the Modified Proctor mold. Samples were immediately tested upon compaction. Four specimens were compacted at different moisture contents with the intent of achieving densities higher than a certain predetermined density. Figure 22 gives the compaction curves obtained from CBR test. A maximum dry density of 1.65 Mg/m^3 was obtained at optimum moisture content of 18%. Figures 23, give the CBR load-displacement relations for the four samples compacted at different moisture content.

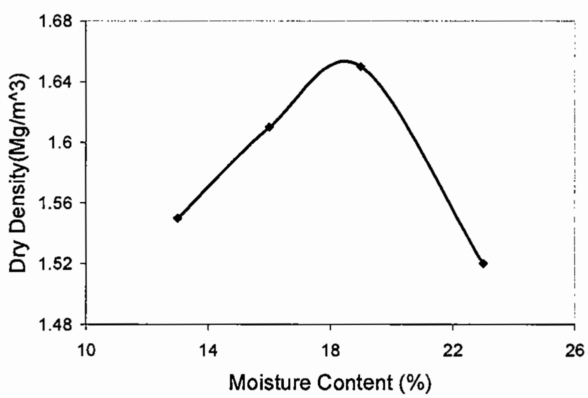


Figure 22: Dry density and moisture content relationship curve based on CBR test.

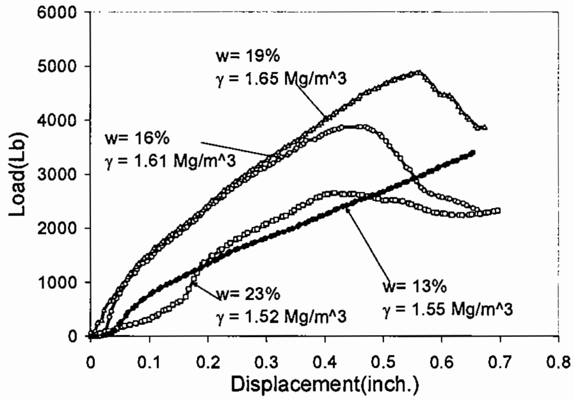
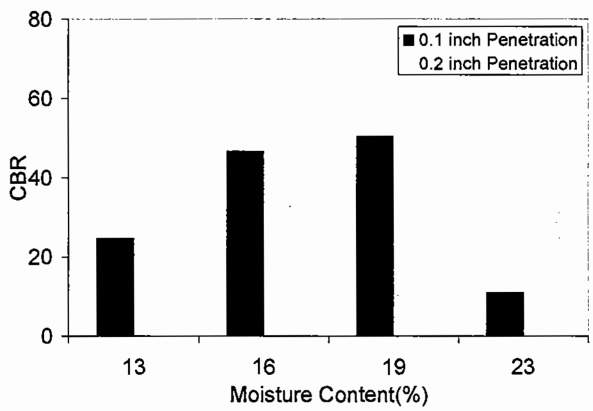


Figure 23. CBR load-displacement relationship for aggregates

(a)



(b)

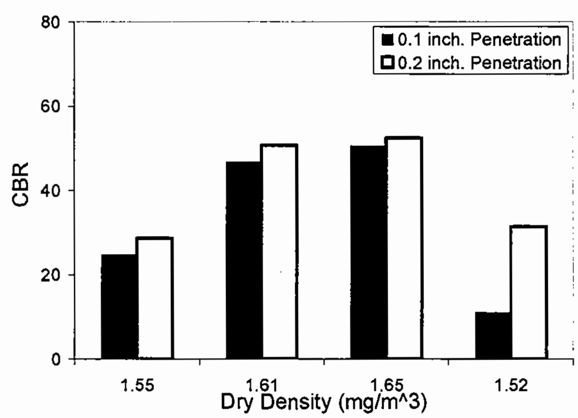


Figure 24. CBR values for aggregates

Figures 24a and 24b give plots of CBR value versus dry density and moisture content for the light weight aggregates tested immediately after compaction. CBR values were in the range of 28 to 52. As seen, the CBR value depends both upon the moisture content and the dry density of the compacted aggregates. Higher moisture content, especially that well above the optimum moisture content, leads to both low dry density as well as low CBR value. Table 6 tabulates the result of CBR values, dry density and moisture content of light weight aggregates

Table 6. Results of fly ashaggregates

Properties		Fly ash
SPT	Maximum Dry Density (Mg/m^3)	1.61
	Optimum Moisture Content (%)	19
Specific Gravity		1.73-1.75
Bulk Specific Gravity Mg/m^3		1.31-1.46
CBR	Optimum Moisture Content (%)	18
	Maximum Dry Density (Mg/m^3)	1.65
	CBR (%)	52
Absorption (%)		20 %- 22%

Ponded Ash Aggregates:

Based upon the literature review, we believe that not only dry scrubber ash but also ponded hydrated class C fly ash may be utilized to produce lightweight aggregates with adequate mechanical properties, such that they may be applied in various construction activities. Consequently, we have documented the following physical and engineering properties: grain size distribution, density, specific gravity, compaction characteristics and the CBR test results, for two samples of ponded fly ashes.

Grain size distributions were obtained from the sieve analysis on two samples of ponded ash. Since the ponded ash brought from the plant was partial hydrated, the particles sized reached up to 35 mm. The samples were first sieved through the 31.5mm, 16mm, 8mm, 4mm and 1 mm sieves according to ASTM C136 to obtain the coarse aggregate grain size distribution. The portion passing 4 mm sieve was then used for fine aggregate sieve analysis according to ASTM C136. Three tests were performed on fine aggregates using sieves with openings: 4.75mm, 2mm, 0.85mm, 0.425mm, 0.25mm, 0.14mm and 0.075mm. The grain size distribution curves obtained from the tests are shown in Figures 25a and 25b.

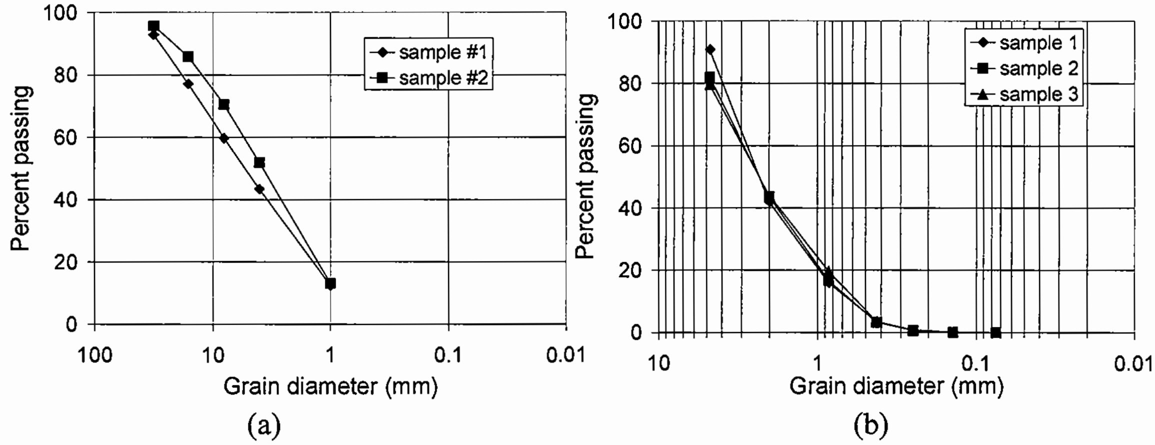


Figure 25. Grain size distribution of ponded ash.

Ponded Ash Sample 1: The density of the ponded ash was determined according to ASTM D 1556, the moisture content test was conducted according to ASTM 2216 and the specific gravity test was conducted according to ASTM 128. The density is obtained to be 1.016 g/cm^3, the moisture content is 27.3%, and specific gravity is 2.56. Furthermore, compaction tests have been performed using both Standard Proctor (ASTM D698) and Modified Proctor (ASTM D1557) test methods on material passing the 3/4-inch sieve. The intent of these tests is to characterize the compaction moisture-density relationships and understand the compactability of these aggregates. The test results are given in Figure 26. The maximum dry density and optimum moisture content based on the Standard Proctor compaction tests are 1.35 g/cm^3 and 28%, while those based upon the Modified Proctor test are 1.41 g/cm^3 and 28%, respectively.

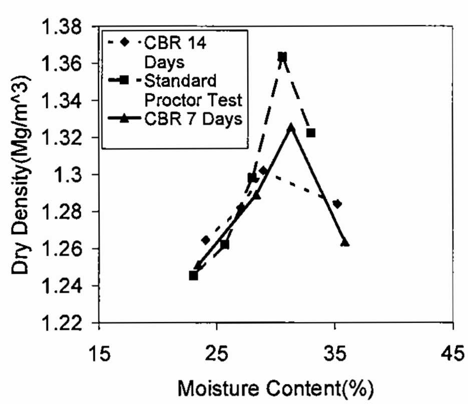
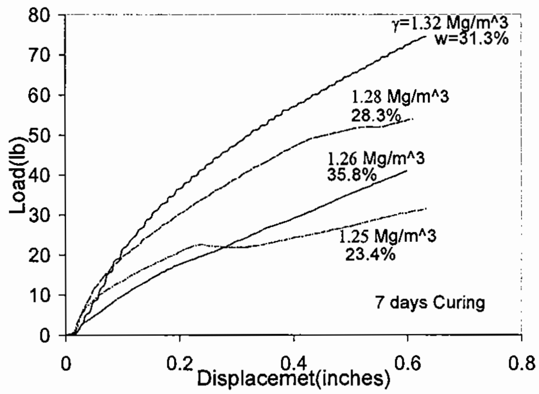
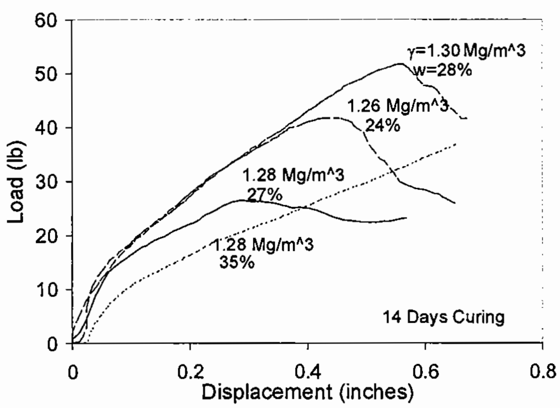


Figure 26. Compaction curves for ponded ash sample 1.

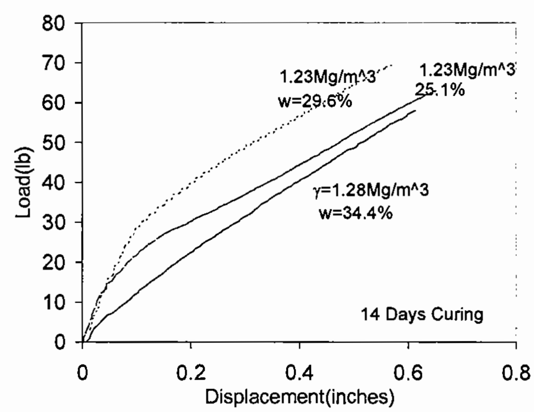
The California Bearing ratio (CBR) test (ASTM D1883) was performed on samples compacted in the Modified Proctor mold and air-cured for 7 and 14-days. Four specimens were compacted at different moisture contents with the intent of achieving densities higher than a certain predetermined density. Figures 27 a, b and c give the CBR load-displacement relations for the four samples.



(a)



(b)



(c)

Figure 27. CBR load-displacement (10^2 lb) relationship for ponded ash sample 1.

The CBR load-displacement relationship is used to obtain the CBR value, which is used as an indicator of performance as a sub-base course material. CBR values greater than 15 indicate an excellent sub-base course material, while CBR values of 5-15 indicate a good sub grade. Class C fly ash used for soil stabilization has shown CBR of as high as 25 (Senol et al. 2002). The specimens were compacted to a density similar to the average density of stabilized soil in the field, and the samples cured in a wet room for seven days before test was performed. Figures 28 and 29 gives the CBR value versus dry density and moisture content for the compacted ponded ash specimens after 7 and 14-day curing. Encouragingly, the CBR values for all the samples are above 30 and may be as high as 82 for favorable moisture and compaction conditions. As seen, the CBR value depends both upon the moisture content and the dry density of the compacted ash. Higher moisture content, especially that well above the optimum moisture content, leads to both low dry density as well as low CBR value. For this ponded ash sample, curing time does not lead to a gain in CBR value. The effect of curing time is not unexpected since fly ashes typically have most strength gain within the first 7-days.

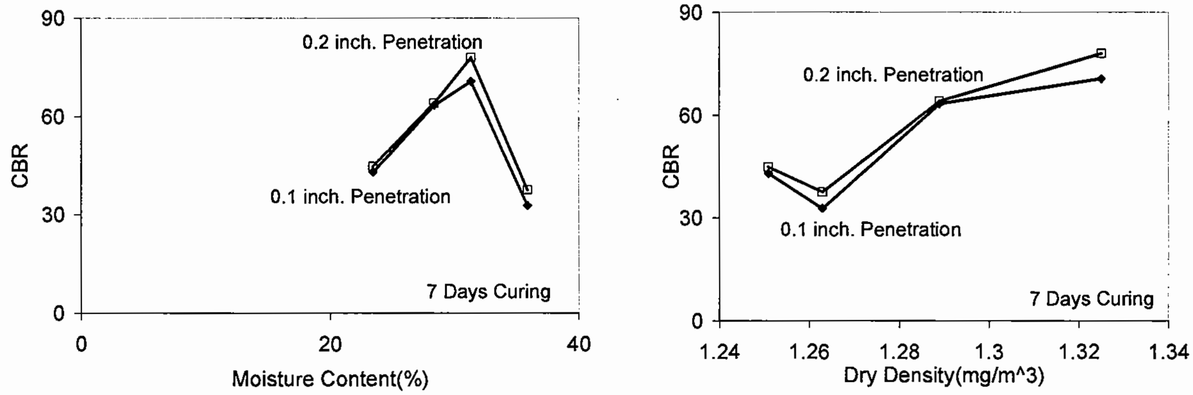


Figure 28. CBR values for 7-day cure for ponded ash sample 1.

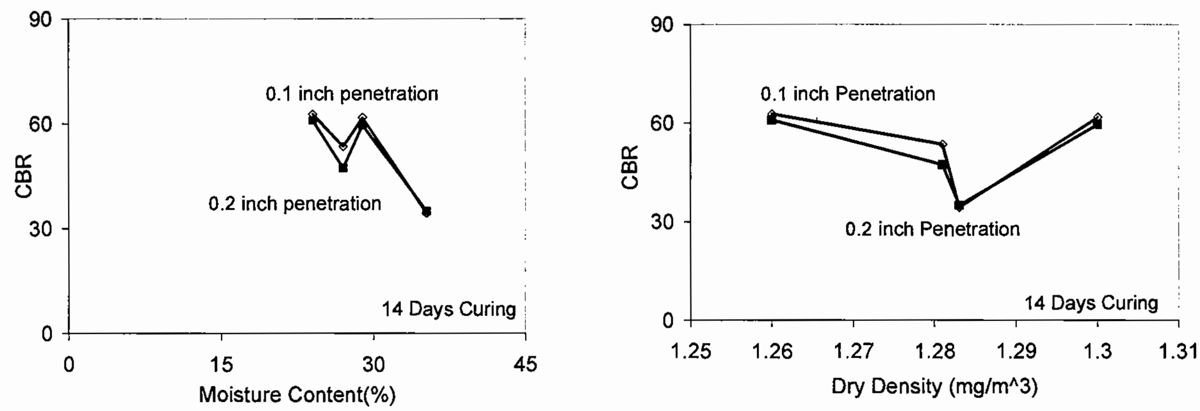


Figure 29. CBR values for 14-day cure for ponded ash sample 1

Ponded Ash Sample 2: The physical properties, such as grain size distribution, density, moisture content and specific gravity are similar to that of sample 1. Compaction tests were performed using both Standard Proctor (ASTM D698) and Modified Proctor (ASTM D1557) test methods on material passing the 3/4-inch sieve. The moisture-density relationship is given in Figure 30. The maximum dry density and optimum moisture content based on the Standard Proctor compaction tests are 1.49 g/cm^3 and 23.47%, while those based upon CBR test sample compaction are 1.50 g/cm^3 and 28%, respectively.

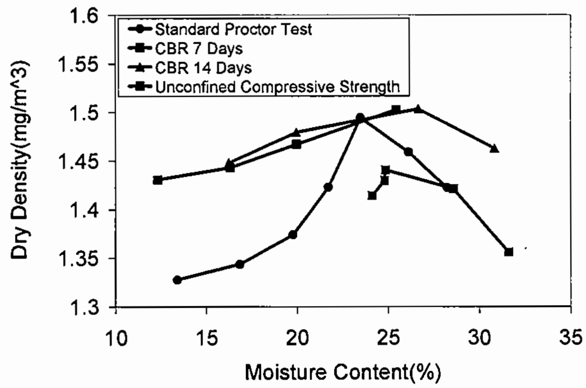


Figure 30. Compaction curves for ponded ash sample 2.

Unconfined compressive strength test was performed on ponded ash by compacting the ash in a 3-inch diameter and 6-inch high mold. The compacted samples were wrapped in a plastic wrap and cured in a humidity chamber at 38°C and 75% humidity. Figure 31 gives a comparison plot between the unconfined compressive strength at 7 days and 14 days curing at optimum moisture content.

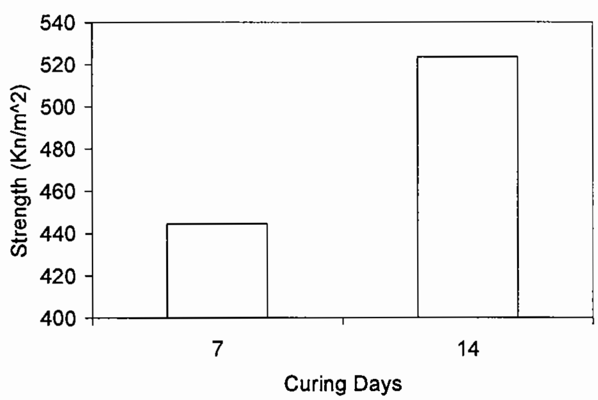


Figure 31. Unconfined compressive strength versus curing days for 7 and 14day cured samples.

The CBR tests were also performed on ponded ash sample 2. Figure 32 gives the CBR load-displacement relationship for 14 days curing and 7 days curing. Interestingly, specimens compacted at higher moisture contents (>~25%) show a ductile behavior in contrast to those compacted at low moisture content which show a brittle behavior characterized by a peak in the load-displacement curve.

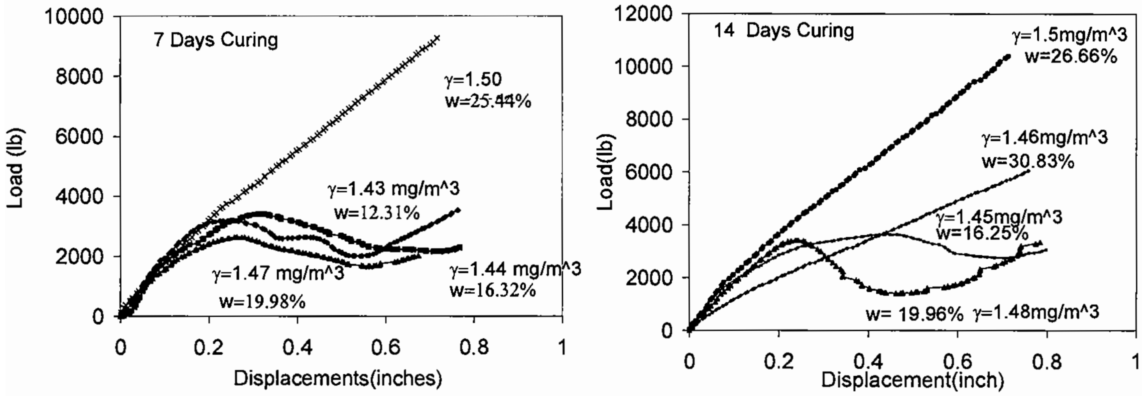


Figure 32. CBR load-displacement relationship for ponded ash sample 2.

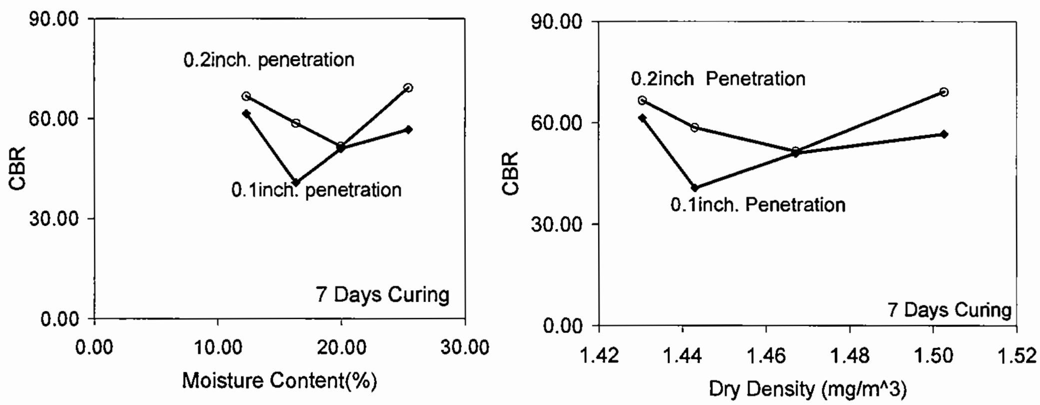


Figure 33. CBR values for 7-day cure for ponded ash sample 2.

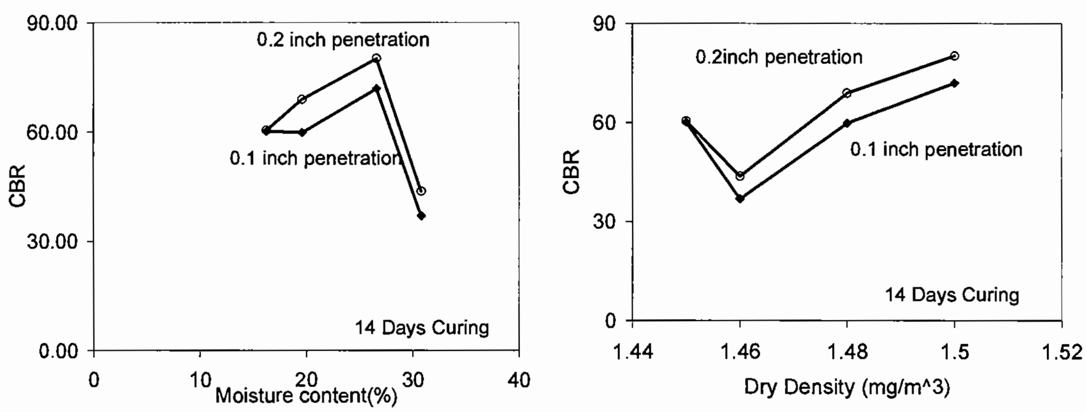


Figure 34. CBR values for 14-day cure for ponded ash sample 2.

CBR and DCP correlation for ponded fly ash

The dynamic cone penetrometer (DCP) test is increasingly utilized for assessing the California bearing ratio (CBR) values. The purpose of this laboratory investigation was to see whether these correlations also exist for ponded fly ash. The testing program to develop CBR-DCP correlations for ponded fly ash included the determination of the following moisture-density relationships of the ponded.fly ash, and California Bearing Ratio (CBR) and Dynamic Cone Penetrometer (DCP) penetration rates. These tests were conducted in accordance with the methods specified by the American Society of Testing and Materials (ASTM) and the American Association of State Highway and Transportation Officials (AASHTO). In this study five samples were prepared at varying moisture contents.

Moisture-Density Relationship

Compaction tests were performed using CBR molds according to (AASHTO T 193-99) test methods on material passing the 19mm sieve. The moisture-density relationship for the ponded fly ash is shown in Figure 35. The maximum dry density is found to be 1.54 Mg/m^3 at optimum moisture content of 23%.

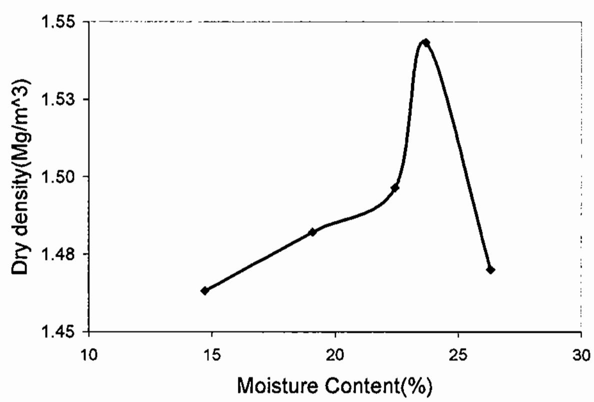


Figure 35. Dry density and moisture content relationships for Ponded fly ash.

California Bearing Ratio

CBR tests were conducted in accordance with the methods described in AASHTO T 193-99, which is the standardized test method. This test measures the resistance to penetration using a loading device such that penetration rate is 0.05 inch/min. As described earlier, the samples were compacted in three layers in the CBR molds at 56 blows per layer. CBR tests were performed for the varying moisture content. The load-displacement data gathered from the CBR tests are plotted in Figure 36. The CBR values obtained from these load-displacement data are tabulated in Table 7. As seen, the CBR values from 95-126 depending upon the moisture content. Also, from the load-displacement curves and the tabulated CBR-values, it may be observed that ponded fly ash experience brittle failure.

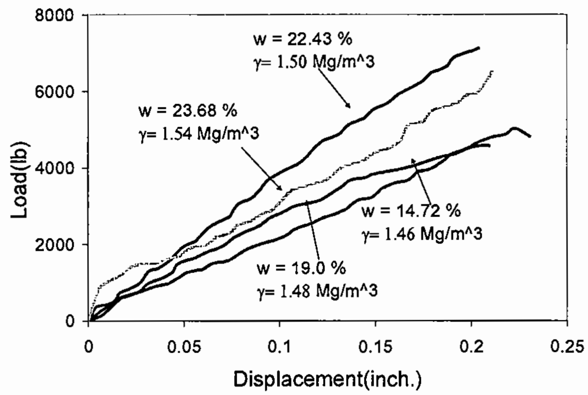


Figure 36. Load-penetration curves for Ponded fly ash.

Table 7. Dry density and CBR values for ponded fly ash at different moisture content.

Test Number	Ponded Fly ash			
	W (%)	γ (Mg/m^3)	CBR (0.1 inch)	CBR (0.2 inch)
1	14.7	1.46	67	95
2	19.08	1.48	91	95
3	22.43	1.50	125	149
4	23.68	1.54	102	125

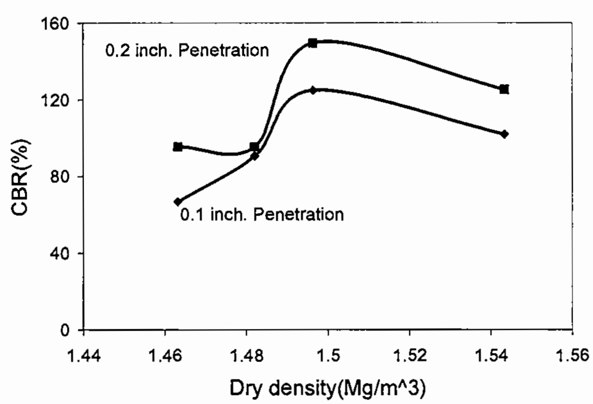


Figure 37. CBR versus dry density

Figure 37 shows plots of CBR with dry density. We observe that the CBR values are, typically, higher for the moisture contents that are less than the optimum moisture contents. From Figure 37 we also note that: for the ponded fly ash, the maximum CBR of 149 corresponds to a dry density of 1.50 Mg/m^3, which is not the maximum dry density. The maximum dry density in this case was 1.54 Mg/m^3 and the corresponding CBR value is 125.

Dynamic Cone Penetrometer Test

The Dynamic Cone Penetrometer (DCP) test was completed using standard testing methods specified in the new ASTM test D6951-03. This test is a measurement of the penetration rate of the dynamic cone penetrometer through an undisturbed soil sample. The standard test uses a DCP device with an 8-kg hammer, which is dropped from a height of 22.6 inches for a given number of blows. The penetration depth of the cone tip into the soil is then recorded for the number of blows. For these experiments, two blows per recording were used with a maximum penetration of 10 cm. For the DCP test, the cumulative penetration is plotted in Figure 38 as a function of cumulative number of blows for each sample. A regression analysis was performed to fit a line to the data points.

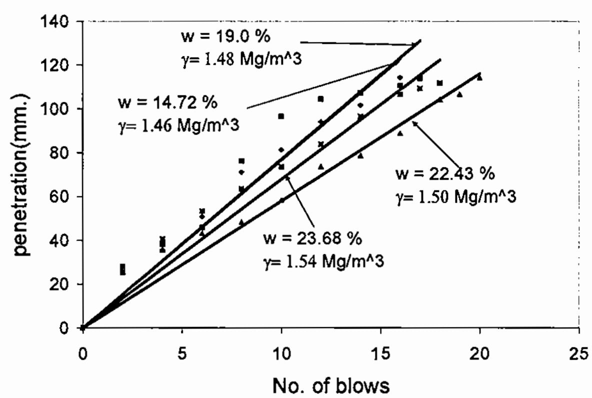


Figure 38. Cumulative penetration versus cumulative number of blows.

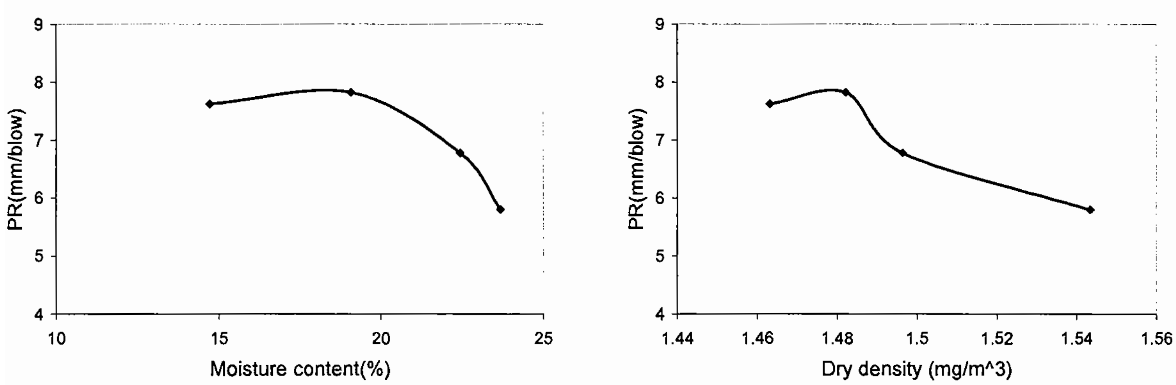


Figure.39 Plot of Penetration Rate (mm/blow) with moisture content and dry density.

Figure 38 shows the dependence of the penetration rate, given by the slopes of the linear fits. From figure 39 it was observed that penetration rate is decreasing with increase in moisture content. Interestingly, the penetration rate was found to decrease rapidly after moisture content of 20 % and dry density of 1.48 Mg/m^3.

Correlation between CBR and DCP Penetration Rate

Figure 40 shows the variation of CBR as a function of the DCP penetration rate measured in the laboratory on a log-log scale. Based upon the linear regression analysis of this data, the following correlations are obtained for CBR and PR (mm/blow):

$$LogCBR = 2.98 - 1..09(LogPR) \qquad (1)$$

The goodness-of-fit coefficient R^2 for these relationships is 0.46. Interestingly, the intercept and slopes for the correlations in Equations 1 are very similar to those for Class C fly ash stabilized clay soils given by Misra et al (2004). The correlation is also similar to that of subgrade materials given by Webster et al. (1992), who obtained an intercept of 2.465 and a slope of 1.12, for a wide range of granular and cohesive materials.

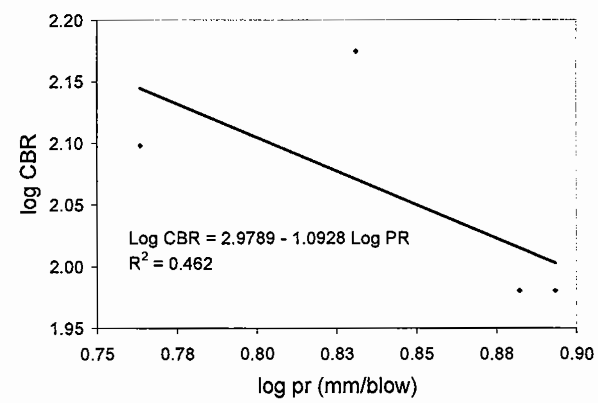


Figure 40. CBR-DCP correlations for ponded fly ash penetration rate data.

Leaching Potential of Fly Ash Aggregates:

Data available in the literature shows that Class C fly ash derived from Wyoming coal, generally, leaches only very small quantities of contaminants of concern (Garcez and Tittlebaum 1984, EPRI 1995). Nevertheless, leaching behavior of each fly ash must be examined on a case-by-case basis in relation to the background water quality. These leaching tests must be standardized with respect to the leaching fluids that best represent the fluids in nature, such as, simulated groundwater or rainwater leachates. In absence of these standards, the TCLP test provides a method for evaluating the leaching potential of a fly ash. Therefore, in this report, the leaching behaviors of the LaCygne ash utilized in this project are examined based upon the TCLP test results. Results of the TCLP tests are give in Table 8 and Figure 41 along with the Drinking Water Standards (DWS) and the RCRA standards. We have included test results from samples obtained in 1994 and 1995, in addition to those in 1998 to demonstrate that the fly ash leaching characteristics are quite uniform.

Table 8: TCPL Test Results – LaCgyne fly ash

Element	LaCygne fly ash (mg/l) TCPL Test				DWS Standards (mg/l)	RCRA Standards (mg/l)
	Sampled 01/15/94	Sampled 02/03/95	Sampled 1998 (10 Samples)			
				Avg		
Lead	<0.05	<0.05	8 samples < 0.05 avg of 2 samples 0.115	0.063	0.05	5
Chromium	0.09	0.18	4 samples < 0.01 avg of 6 samples 0.158	0.098	0.05	5
Cadium	<0.01	<0.01	8 samples < 0.01 avg of 2 samples 0.205	0.049	0.01	1
Barium	0.76	0.5	avg of 10 samples 0.534	0.534	1	100
Sliver	<0.03	<0.02	10 samples < 0.02	<0.02	0.05	5
Selenium	0.224	0.19	5 samples < 0.01 avg of 5 samples 0.214	0.112	0.01	5
Arsenic	0.048	0.12	5 samples < 0.01 avg of 5 samples 0.018	0.014	0.05	5
Mercury	<0.0002	<0.005	10 samples < 0.005	< 0.005	0.002	0.2

As shown in Table 8 and Figure 41, none of contaminants of concern exceed the RCRA standards. Data from literature indicates that it is quite likely that the extracted concentrations of the various contaminants are highest in the TCLP test. Thus in most cases these TCLP numbers represent the worst case scenario and may be used to judge the leaching potential of the fly ash. Quite clearly, the ash utilized in this project leach very low quantities of most contaminants of concern.

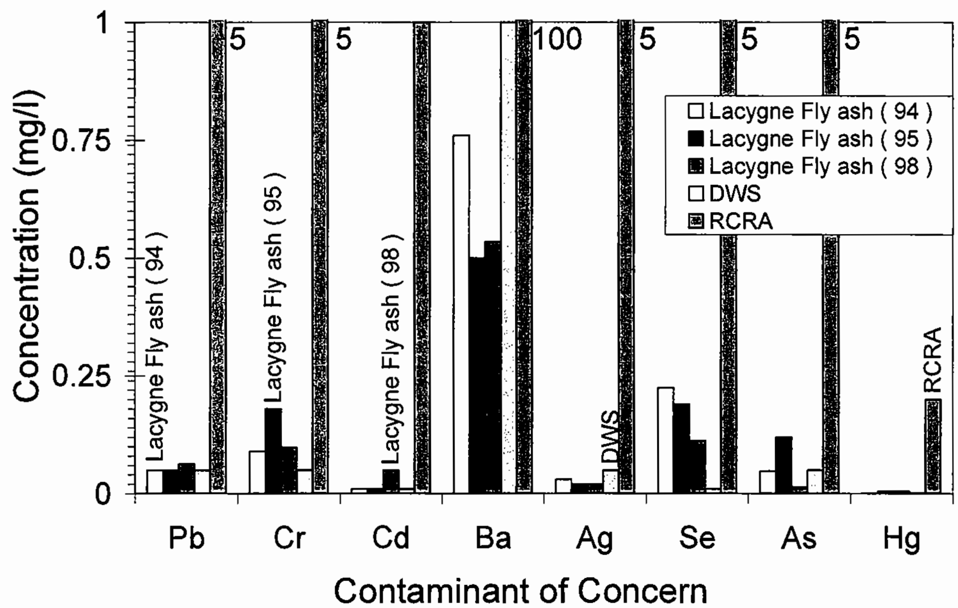


Figure 41. Leaching behavior of LaCygne Class C fly ash

V. SUMMARY AND CONCLUSIONS

Literature review

A literature search was performed with a focus upon collecting, reviewing, analyzing and summarizing available information concerning: (1) appropriate cut strand fibers and fiber fillers that may be used for ash-fiber-sand aggregate production; (2) the utilization of class C fly ash for aggregate production; (3) other efforts to produce synthetic aggregates, especially those using cementitious materials; and (4) characterization methods for aggregates in various construction applications.

Based upon the literature review, we have noted that little effort has been made to exploit the self-cementing capacity of fly ashes for producing aggregates. Most fly ash aggregate production methods employ some type of high temperature sintering process. A few efforts that have aimed at producing unsintered aggregates have yielded encouraging results. Therefore, we believe that the self-cementing properties of class C fly ashes can be exploited to produce lightweight aggregates with adequate mechanical properties, such that they may be utilized in various construction activities.

Fly ash-fiber-sand mix proportions

Based upon the literature review and cost and availability of appropriate fibers, three candidate fiber fillers were selected for ash-fiber-sand mixes. Fine sand was sieved from locally available construction sand. 2-inch cube samples for several fly ash-sand-fiber mix proportions were prepared by varying the fiber content. The cubes were allowed to harden for 1 day in a moisture cabinet, then de-molded and cured for at least 7 days in an environmentally controlled chamber. Unconfined compressive strength test is performed to obtain the 7-day compressive strength.

Based upon the tests performed, the optimal mix proportion for water-fly ash-sand mortar was found to be 0.3:1.0:2.0. Under controlled curing, this mortar proportion yields an average 7-day compressive strength of 14.6 MPa, with a coefficient of variability of less than 10%. Moreover, the addition of fibers, generally, results in a higher modulus of elasticity, however, the behavior for different fiber types are different. Optimal fiber content is, therefore, a function of the fiber type and we expect to define that content for the three fiber types selected for the proposed project. Based upon the strength results, mixtures with the glass fibers at 15% replacement rates yield the best strength.

Characterization of fly ash-fiber-sand aggregate engineering properties

Using the optimal mix proportion and fiber type, batches of fly ash-fiber-sand aggregate have been extruded. The extruded aggregates were used to perform particle shape and surface texture tests, gradation tests (ASTM C136), moisture absorption capacity, and specific gravity and density tests (ASTM C29 and ASTM C127). The aggregates had very high absorption capacity and also had a propensity to abrade easily. Consequently, the mix proportion was modified and additional aggregate batches extruded. These aggregates were then used to perform particle shape and surface texture tests, gradation tests (ASTM C136), moisture absorption capacity, specific gravity and density tests (ASTM C29 and ASTM C127) and finally soundness and durability tests (ASTM C88 and AASHTO T103). The results show that aggregates meet the properties of base course and sub-grade material, however, the soundness and durability performance were not up to the specification. Low sulfate resistance could be due to high absorption capacity, which in-turn may be a caused by the sand content. Consequently, the mix proportion and the production technique were revised to reduce the porosity of the aggregates. The sand content was reduced and the fiber content was increased. Extruded aggregates using the new mix-proportion were prepared and found to have improved absorption capacity. These aggregates were also found to be susceptible to sulfate attack, which could also be attributed to the somewhat high absorption capacity. Therefore, it was decided to completely eliminate sand from the mix and produce crushed samples from samples that have been compacted.

A production methodology that considers pressure compacted samples with precision moisture control which are subsequently oven cured at low temperature was also evaluated.

Three methods of crushed aggregate production based upon compacted samples were investigated. After examining the grain size distribution of different kinds of crushed aggregates made with the above procedures, we concluded that the aggregates made using procedure 1 have an applicable grain size distribution. Moreover, procedure 1 is expected to be more economical compared to the other two procedures, which require sintering at 850 °C. Therefore, the less energy intensive procedure 1 was further investigated for aggregate production. Fly ash briquettes were compacted using this compaction methodology. These briquettes were crushed to produce sufficient amount of aggregate for investigating the aggregate properties for its application. Grain size distribution, specific gravity and bulk density, and particle shape and texture were determined. The moisture-density relationship and the CBR values were also determined. The specific gravity of these aggregates are 1.73-1.75 and the maximum compacted dry density is ~1.6 Mg/m^3. Thus, these aggregates fall within the category of lightweight aggregates. The CBR values are obtained in the range of 28-52 depending upon the compaction moisture content. Even at low CBR values of 28, the compacted aggregate material would provide a competent road base or sub-base.

Characterization of ponded ash aggregate engineering properties

The above results indicate that ponded class C fly ashes could yield a rich source of crushed aggregates that may be used for road bases, lightweight embankment fills as well as lightweight granular backfills behind retaining walls. A number of tests were performed to characterize crushed aggregates derived from ponded fly ashes. We have documented the following physical and engineering properties: grain size distribution, density, specific gravity, compaction characteristics and the CBR test results, for two samples of ponded fly ashes. The density of ponded ash is found to be low, thus it would result in a lightweight road base/sub-base material. The CBR values are obtained in the range of 40-90 depending upon the compaction moisture content. Even at low CBR values of 40, the compacted ponded ash material would provide a competent road base or sub-base. We have also found that the 14-day cured samples provided higher values than the 7-day cured samples, indicating that the ponded ash have some residual cementation capacity. Given that the 7-day strengths and CBR values are sufficiently high for road base or sub-base applications, it is expected that ponded ash will provide even better performance in the long-term.

Fly ash aggregate leaching behavior

Leaching tests have been performed on the fly ash using the TCLP procedure. TCLP test result show that the self cementing fly ash utilized in this project leach very low quantities of most contaminants of concern. Since TCLP test likely represents the worst case scenario, the leaching potential of contaminants of concern from the fly ash aggregates is expected to be low.

VI. References

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