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Project Title: USE OF FLY-ASH BASED BINDERS FOR FOUNDRY MOLDS

ICCI Project Number: 96-1/3.1A-1
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ABSTRACT

Fly-ash disposal from coal combustion is a serious problem for coal-fired power plants. Some means is therefore needed for disposing of or utilizing the fly-ash. Of the tremendous amounts of fly-ash produced each year, only a small fraction can be used constructively in useful applications, while the majority of fly-ash is landfilled. The beneficial use of fly-ash in an economical and environmentally acceptable manner is important for encouraging the continued use of Illinois coals.

The objective of this project was to develop a new class of markets for Illinois fly-ashes, as particulate binders for the production of sand molds in foundry operations. Each year U.S. foundries consume over 885,00 tons of binder for producing metal-casting molds. The ability to use fly-ash as a binder in the production of foundry molds would consume considerable amounts of Illinois fly-ash, but to this date no studies have been conducted using fly-ash in this application. The extensive Illinois foundry industry would benefit from being able to use locally produced fly-ashes as binders to replace the bentonite, which must be shipped long distances.

In this project, the necessary parameters for producing satisfactory fly-ash bonded foundry molds were determined. All of the fly-ashes studied could be used as satisfactory binders, provided that calcium chloride was added as an accelerator for the binding reactions. The ash from a fluid-bed combustor functioned as a binder with only calcium chloride and water added, but the Class F fly-ashes required additions of calcium-bearing compounds, preferably CaO, before they exhibited binding properties. All of the ash-based binders performed best when they were first pre-reacted with water before adding them to the sand. Molding sand specimens also had the best properties when they were rammed, and then cured for one hour before testing. Fly-ash bonded sands also had satisfactory performance when heated to elevated temperatures, showing that they would behave properly in contact with molten metals in casting operations. The necessary conditions for using fly-ash as foundry sand binders have been established, and prospects for successfully casting metal parts using these sand binders are very good.

EXECUTIVE SUMMARY

Fly-ash is produced in great quantities as a by-product during the combustion of coal, primarily by coal-fired power plants. It is entrained in the exhaust gases and would create a serious dust problem in the surrounding area if released, so clean-air guidelines require that the fly-ash be collected from the flue gases. It is obviously preferable to market the fly-ash for useful purposes instead of simply landfilling it, since the market price can help to defray the costs of shipping and handling the material.

The main existing market for fly-ash is as a cement additive. However, this market requires that the fly-ash contain less than 6% unburned carbon by weight, and a large percentage of the fly-ash produced in the U. S. contains more than 6% unburned carbon. These large quantities of high-carbon fly-ashes have little or no commercial application and must be disposed of in landfills. Therefore, applications in which a high carbon content is non-critical, or even desirable, must be developed for these fly-ashes. An application in which high levels of carbon or other impurities would be desirable is as an inorganic binder to replace or supplement bentonite clay, which is used in foundries to produce sand molds in the casting of metal components. Previous work conducted by the investigators had determined that high-carbon fly-ashes with carbon contents as high as 11.1% can be used as inorganic binders.

A useful binder for foundry sands must be able to hold sand particles together strongly enough to produce molds that can hold their shape and surface detail while molten metal is poured into them. The binder must also give the mold sufficient permeability to allow gases to escape without producing casting flaws. In addition, the molds must be able to withstand high temperatures, without melting into a mass that would be difficult to remove from the finished part. Experimentation carried out by this project to date has concentrated on determining whether binders based on fly-ash can match the baseline characteristics obtained with a conventional bentonite binder, which is known to produce acceptable-quality foundry molds.

The fly-ashes used to date were obtained from a fluidized-bed combustor operated by ADM, Inc. in Decatur, Illinois, and from the pulverized-coal combustors at the E.D. Edwards plant, operated by the Central Illinois Light Co. The ADM fly-ash is a very high-calcium, moderately high-carbon fly-ash that also has a high sulfate content, all of which tend to make it unusable in existing fly-ash applications. The plant therefore must currently dispose of it by landfilling. The Edwards plant produces fly-ashes containing 6.87% carbon and 11.11% carbon which have low calcium and sulfate contents compared to ADM fly-ash, but their carbon contents are still high enough to make them unusable in existing fly-ash applications. The compositions of the ashes studied are given in Table 1.

The sand used in these experiments was a standard foundry grade with an AFS grain fineness number of 55, which was provided by a midwestern sand producer at no charge to the project. This is a sand that is currently being used by the Caterpillar foundries, as well as many other foundries in the U. S.

Fly-ash binders were combined with the sand, and the mixture was formed into standard forms for testing. A summary of the tests and their purposes is given in Table 2.

In this project, it was determined that compressive strength and shear strength of foundry

Table 1: Chemical analyses of the Illinois fly-ashes being used, with the analysis of a typical western bentonite included for comparison.

Compound	ADM Fluid Bed Combustor	Edwards Dry Low Carbon	Edwards Dry High Carbon	Western Bentonite
SiO_2	19.62	50.07	48.00	39.62
Al_2O_3	6.60	24.41	23.87	23.16
Fe_2O_3	5.04	9.51	9.34	5.49
$SiO_2+Al_2O_3+Fe_2O_3$	31.26	83.99	81.21	68.27
CaO	46.19	2.72	2.63	9.63
MgO	3.33	0.85	0.84	2.11
Na_2O	0.69	0.61	0.55	1.06
K_2O	0.81	2.68	2.61	0.39
TiO_2	0.43	1.22	1.25	1.25
MnO_2	0.13	0.05	0.05	0.01
P_2O_5	0.72	0.09	0.12	2.20
SrO	0.08	0.15	0.14	0.39
BaO	0.05	0.16	0.16	0.53
SO_3	12.53	0.61	0.54	5.93
Loss On Ignition	3.08	6.87	11.11	13.24

sand/binder mixtures were strongly affected not only by the dosage of fly-ash, but also by the moisture content, and by the dosage of calcium chloride which was added as a curing accelerator. It was also found that the quality of the bonded sand specimens could be greatly improved by reacting the fly-ash with calcium chloride and water for 20 minutes before mixing it with the sand, and by allowing the specimens to cure at room temperature for 1 hour before testing for compressive and shear strength.

Experiments were then conducted to determine the effects of variations in moisture content on the sand specimen properties. The ADM fly-ash was added at a constant dosage of 10% of the sand weight in all the tests where it was used. The Edwards fly-ashes were added at a constant dosage of 6% of the sand weight, along with supplemental calcium in the form of either calcium oxide (at a dosage of 4% of the sand weight) or calcium hydroxide (at a dosage of 5.28% of the sand weight). All experiments included calcium chloride as a curing accelerator, added at a dosage of 3% of the sand weight. The fly-ash results were compared to the baseline results obtained earlier using bentonite binder added at a dosage of 6% of the sand weight, with 2% moisture.

Permeability was found to be a strong function of the moisture content, with the highest

Table 2: Description of tests used to evaluate the properties of molded sand test samples. These are standard tests for foundry sands, recommended by the American Foundrymen's Society (AFS).

Test	Procedure	Use of Data
Compressive Strength (Green)	A compressive load is applied to a cylinder of compacted sand until the cylinder fails.	Determines the maximum compressive stress a mixture is capable of sustaining when rammed into a mold. The ability of a mold to hold together is dependent on this parameter.
Permeability	Air is forced through a cylinder of compacted sand inside a metal sleeve, and the permeability determined from the flowrate and pressure drop.	Measures the flow of gasses through a porous media such as compacted or cured molding sand. Venting qualities of a sand mold are dependent on this quality.
Moisture Content	A 50g sample of uncompacted sand is placed in a hot air dryer for seven minutes at 110°C to remove the moisture from the sand. Moisture is determined from the loss in weight of the sample.	Used in determining the amount of water needed to properly make a sand mold hold a form without interfering with any of the other mold properties.
Shear Strength (Green)	A cylinder of compacted sand is placed in a pendulum type strength machine and a diametric load is applied to the opposite halves until the specimen shears.	Determines the maximum shear stress a sand mixture is capable of sustaining when rammed into a mold. The ability of a mold to hold pattern details is dependent on this parameter.
Compactability	Sand is de-lumped through a 6.35 mm screen into a sample cylinder, any excess sand is removed, taking care not to compact the sand. The specimen tube is compressed by a 140 psi load. The percent change in height is used to determine compactability.	Determines how much a sand will compact when a load is applied to it. If the sand has poor compaction properties, it will be difficult to ram into a mold, and may deform when metal is poured, producing a poor-quality casting.

permeability achieved at a moisture content of approximately 3.5% for the ADM ash, and at 4% for the Edwards ash. The ADM ash reached a maximum permeability that was comparable to that of the bentonite binder, while the permeabilities for the Edwards ash were significantly lower.

Increasing water addition also increased the compressive strength. The compressive strength with no curing time reached its maximum at 4% moisture for the ADM ash and the Edwards ash with calcium hydroxide, and at nearly 5% moisture for the Edwards ash with calcium oxide. Before curing, the Edwards ash with calcium oxide showed a higher strength than the Edwards ash with calcium hydroxide, indicating that calcium oxide is a better choice for a calcium source than calcium hydroxide. After providing a one hour curing time, the compressive strengths increased for all of the binders tested, which all equalled or exceeded 50 psi between 4.0% and 4.5% moisture.

Shear strength of the test specimens was too low to be reliably measured for all of the fly-ash bonded specimens when no curing time was provided. However, when a one hour curing time was used, the shear strength increased. At moisture contents greater than about 3.0 - 3.5%, the cured shear strength was higher than the shear strength obtained with a bentonite binder.

From these studies, it was concluded that the fly-ash binders require moisture contents of 3.5 - 4.0% for the best permeability, and 4.0 - 5.0% for the best compressive and shear strengths. Experiments were also conducted to compare the temperature resistance of fly-ash-bonded sand specimens to that of bentonite-bonded sand specimens. Upon heating to 600°C and 1000°C, the fly-ash-bonded specimens maintained their strength, without premature melting problems. The results were comparable to those seen using a bentonite binder.

The Class F fly-ashes used in this project had carbon contents of 6.87% and 11.11% by weight. Using these ashes, experiments were conducted to determine the effects of carbon content on the properties of the bonded sand. The carbon content was shown to have no harmful effect on the sand specimen properties, which indicates that fly-ashes with a broad range of carbon contents can be readily used in this application.

Fly-ash binders have been demonstrated to have properties suitable for use as foundry sand binders. With proper addition rates and handling, they can produce bonded sand properties comparable to those produced with conventional bentonite binders. The prospects for successful use of fly-ash binders to produce actual cast metal parts in foundry operations are therefore excellent.

OBJECTIVES

The ultimate goal of this project is to develop a new application for fly-ashes. This application is as a binder for the sand molds used in foundries for casting metal, a market which consumed 885,000 tons of binder in the U. S. in 1995. To accomplish this goal, the following objectives are planned:

- Determine the compositions of fly-ash that provide the most useful properties for foundry operations.
- Determine the fly-ash based binder concentration that gives the best combination of strength, heat resistance, recyclability, and mold permeability.
- Demonstrate the use of fly-ash based binders in sand molds, and evaluate the quality of the metal casting specimens produced.

INTRODUCTION AND BACKGROUND

Fly-ash is produced in great quantities by Illinois power plants as a residue of coal combustion. The ash is collected from the plant flue gases, usually by electrostatic separation, and must then be discarded. Some fly-ashes can be marketed as cement admixtures, but the majority have unsuitable compositions, and so must be disposed of by landfilling. The major problems are high-carbon fly-ashes, and fly-ashes from fluidized bed combustors, neither of which have any existing markets of any consequence.

The goal of this project is to find an application where the carbon content of the fly-ash is either not a problem, or is a desirable feature. The application being studied is as a binder for the molding sands used by metal foundries.

In metal-casting operations, sand is used to make molds for the molten metal. The sand is combined with binders that allow the molds to keep their shape when the hot metal is poured into them, and that also allow easy removal of the sand mold after the metal solidifies. Typically the amount of binder used is between 2% and 50% of the weight of the sand, and the U. S. Geological Survey estimated that 885,000 tons of binder was used in this application in the U. S. in 1995.[1] Use of fly-ash as a foundry sand binder would therefore be able to utilize a significant amount of Illinois fly-ashes, but no studies have ever been conducted using fly-ash as binders for foundry molds.

In a previous ICCI-funded project, it has been found that a mixture of fly-ash, lime, and small amounts of accelerants such as calcium chloride can be used as a binder for production of iron-ore pellets. These fly-ash-based binders have been found to have the following necessary characteristics for use as binders in foundry sand: (1) Resistant to high temperatures; (2) Low cost; and (3)Friable enough to allow the sand to be easily removed from the finished part. It is also expected that they can provide the necessary flowability and compactability needed for foundry sand, and that they will allow the sand to be easily recycled in the foundry operations. From the work that has been done at MTU, it has been found that fly-ashes that are not usable as cement admixtures or in other existing fly-ash markets, can be used as particulate binders. In particular, ashes that are

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1. US Geological Survey (1996), Mineral Commodity Summaries, available by World-Wide-Web, http://minerals.er.usgs.gov:80/minerals/pubs/mcs/clays.txt

high in carbon, or that are produced by fluid-bed combustors, will be suitable for this application. The use of fly-ash in foundry sand binders will therefore make it possible to utilize fly-ashes that currently must be disposed of by landfilling.

This represents a tremendous market for Illinois fly-ashes, as there are 237 foundries in Illinois alone, and approximately 3250 foundries nationwide.[1] The fly-ash would be partially or completely replacing the current binder, bentonite, which costs \$20/ton, and must be shipped from distant mines in Wyoming at an additional cost of approximately \$15-\$30/ton. Since the fly-ash is produced quite near the industrialized areas where foundries are operated, and the fly-ash is currently a waste material, both the base cost and the shipping costs for fly-ash-based binders will be much lower than for bentonite binders.

Factorially-designed experiments were carried out to study the ability of fly-ash to act as a binding agent in the production of foundry molds. Calcium chloride was chosen as the hardening accelerator to be used in these experiments.

In the production of sand molds for foundries, there are several parameters which must be controlled:

- **Permeability**, which is a measure of the ease with which gases flow through compacted molding sand. The ability of trapped gases to escape from a mold, allowing metal to completely fill the mold cavity, depend on this parameter.
- **(Green) Compressive strength**, which is the maximum compressive stress a mixture is capable of sustaining when rammed into a mold.
- **(Green) Shear Strength**, which is the maximum shear stress a sand mixture is capable of sustaining when rammed into a mold.
- **Compactibility**, which is a measure of the percent decrease in height of a loose mass of sand under a fixed compaction force.
- **Moisture Content**, which is the amount of water contained in the sand/binder mixture. Some water is necessary to allow the binder to hold the sand together, but excessive amounts of water cause the sand to flow and reduce the permeability.

Some common terms used in the foundry industry, which arise in discussion of the standard tests, are as follows:

- **Mold**: a mass of sand with a shaped cavity, which molten metal can be poured into to make a part. Molds are made from bonded sand, and are broken free from the part after the metal solidifies.
- **Pattern**: The object that is to be duplicated by the cast part. Patterns are generally made of wood for castings made in bonded sand molds.
- **Ramming**: packing the sand around the pattern, to make a mold.
- **Riddling**: screening sand to break up lumps and remove foreign matter.

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1. American Foundrymen's Society, Personal Communication, May 1, 1996

EXPERIMENTAL PROCEDURES

Materials

The sand used in these experiments was a standard industrial foundry sand, with the size distribution as shown in Table 1.

Table 1: Size distribution of the foundry sand used in this project.

Screen size		Percent weight	
U. S. Mesh	Micrometers	Retained	Cumulative Passing
30	600	0.17	99.83
40	425	6.90	92.93
50	300	30.93	62.00
70	212	33.56	28.44
100	150	20.62	7.82
140	106	6.73	1.09
200	75	0.80	0.29
270	53	0.23	0.06

The fly-ashes used as binders in these tests were:

- A high-calcium fly-ash produced by the Archer Daniels Midland fluid bed combustor in Decatur, Illinois.
- A relatively low-carbon fly-ash produced by the Central Illinois Light Company's E. D. Edwards plant from a conventional pulverized-coal combustor.
- A high carbon fly-ash produced by the E. D. Edwards plant from a Low-NOx combustor

The chemical compositions of these fly-ashes are shown in Table 1.

Granulated reagent grade $CaCl_2•2H_2O$ (98% purity) was added to both fly-ashes as an accelerator for the hardening reaction. In addition to adding $CaCl_2•2H_2O$ to the Edwards fly-ash, reagent grade CaO and $Ca(OH)_2$ (both 98% purity) were added separately to the fly-ash to raise the CaO content to a level that was comparable to that in the ADM fly-ash.

Equipment

In the course of the project, it was found that the binding properties of the fly-ash depend on the conditions under which it is hydrated. Specifically, the hydration process was temperature sensitive, and a method was needed for controlling the temperature of the fly-ash/calcium chloride/water mixture during the hydration process. Therefore, an insulated reaction vessel was used to provide a consistent fly-ash temperature profile during hydration. The vessel consisted of a metal bowl enclosed inside a polystyrene foam container, as shown in Figure 1. The area under the metal pan was lined with insulation in order to fill the void between the bottom of the reaction vessel and the underside of the metal pan. The reaction vessel's lid was also made of polystyrene foam to minimize heat loss to the environment, with a small opening for insertion of a thermometer for measuring and recording the temperature of the binder mixture.

The fly-ash, sand, water, and accelerator were mixed using a Blauknetht counter rotating mixer, with the following characteristics:

- Bowl inside diameter: 12.71 in. (32.3 cm)
- Bowl depth 10.43 in. (26.5 cm)
- Impeller speed: 950 rpm
- Bowl speed: 37.5 rpm

Experimental Procedure

Each experiment consisted of first preparing the sand/binder mixture, using approximately 6.5 kg of sand and the corresponding quantities of binder components. Standard test specimens were then made and used for determining properties such as compressive strength, shear strength, permeability, compactability, and moisture content.

Sand and Binder Preparation. Sand was received in 100 pound (45.4 kg) bags. It was prepared for testing using a riffle splitter, with each bag of sand divided into 8 representative samples, with the weights of each individual sample being recorded.

For each experiment, the desired amounts of sand, fly-ash, calcium chloride, and water were calculated, and the mixture was prepared using the following procedure:

- The sand sample was weighed, and the weight recorded.
- The prepared fly ash sample, $CaCl_2$ sample, H_2O, and any additional calcium compounds were weighed, and the weights recorded.
- Water was added to the insulated reaction vessel (Figure 1), then $CaCl_2$ was added to the water, mixed for 30 seconds to dissolve the $CaCl_2$, and the temperature was recorded.
- The fly-ash (and supplemental calcium, if used) was added to the water and calcium chloride in the insulated reaction vessel, and mixed for 90 seconds to remove lumps.
- The reaction vessel was closed, and the temperature was recorded every two minutes for the duration of the reaction initiation time (ultimately set at 20 minutes).
- After the desired reaction initiation time had lapsed, the fly-ash mixture was removed from the insulated vessel, then added to the sand in the mixing bowl and mixed manually for 30 seconds.
- The mixing bowl contents were mixed using the Blauknetht counter-rotating mixer for 4 minutes.
- After removing from the mixer, the sand/binder mixture was kept covered to prevent loss of moisture.

Preparation of Standard Bonded Sand Specimens. The mixture of sand and binder was used to prepare standard specimen cylinders, which were used for determination of compressive strength, shear strength, and permeability. These cylinders were prepared as follows:

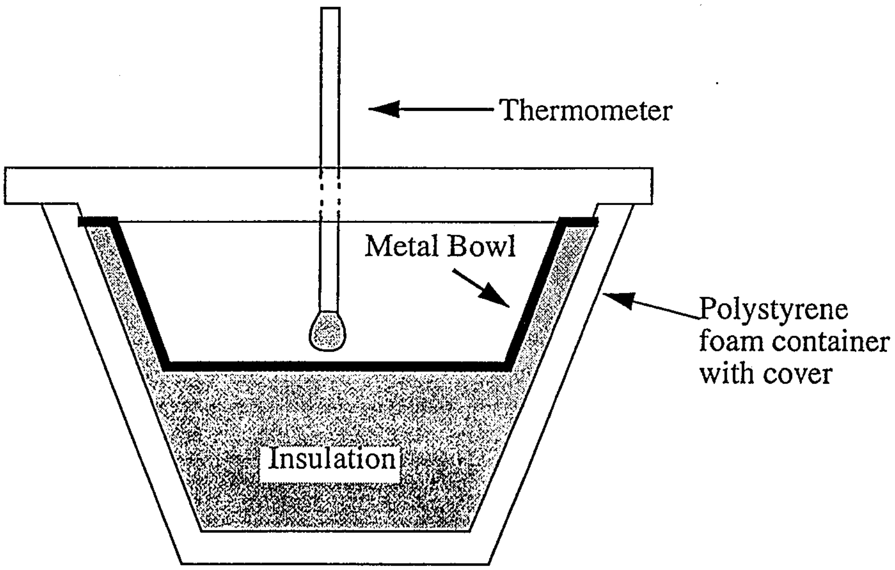


Figure 1. Insulated vessel in which fly-ash slurry hydrates under controlled conditions

- A sufficient quantity of sand/binder mix was weighed into a tared container to produce a cylinder of the desired size (the amount varied depending on the compactability of the sand, and so this value was determined by trial and error).
- The specimen tube and base cap were placed under the rammer assembly (Figure 2), and the weight was slowly lowered to rest upon the sand. The weight was then lifted and dropped a calibrated height to strike the sample 3 times. If the finished specimen height was outside of tolerances (2 in. ± 0.03125 in.), it was discarded, and the amount of sand used for the next specimen was adjusted accordingly.
- Nine specimens were produced from each batch of sand. Six of these were placed in a shallow pan exposed to air and allowed to cure for the desired time before testing. Curing time was ultimately set at 1 hour. The remaining specimens were used for compression tests without curing, and the moisture content of the sand was determined. A summary of the tests used is given in Table 2 of the Executive Summary, and complete details of these tests are specified by the American Foundrymen's Society (AFS).

Experimental Procedure and Results

Initially, a series of factorial-design experiments were conducted to determine the effects of varying ADM fly-ash dosage, moisture content, and calcium chloride dosage on the properties of foundry sand. These results were compared with a baseline experiment which used bentonite binder at a dosage that was known to give satisfactory sand properties. These experiments were used to choose the ranges of compositions that would be used in later work. In these experiments, it was also noted that the compressive strength of fly-ash-bonded specimens increased if they were allowed to cure in air before testing.

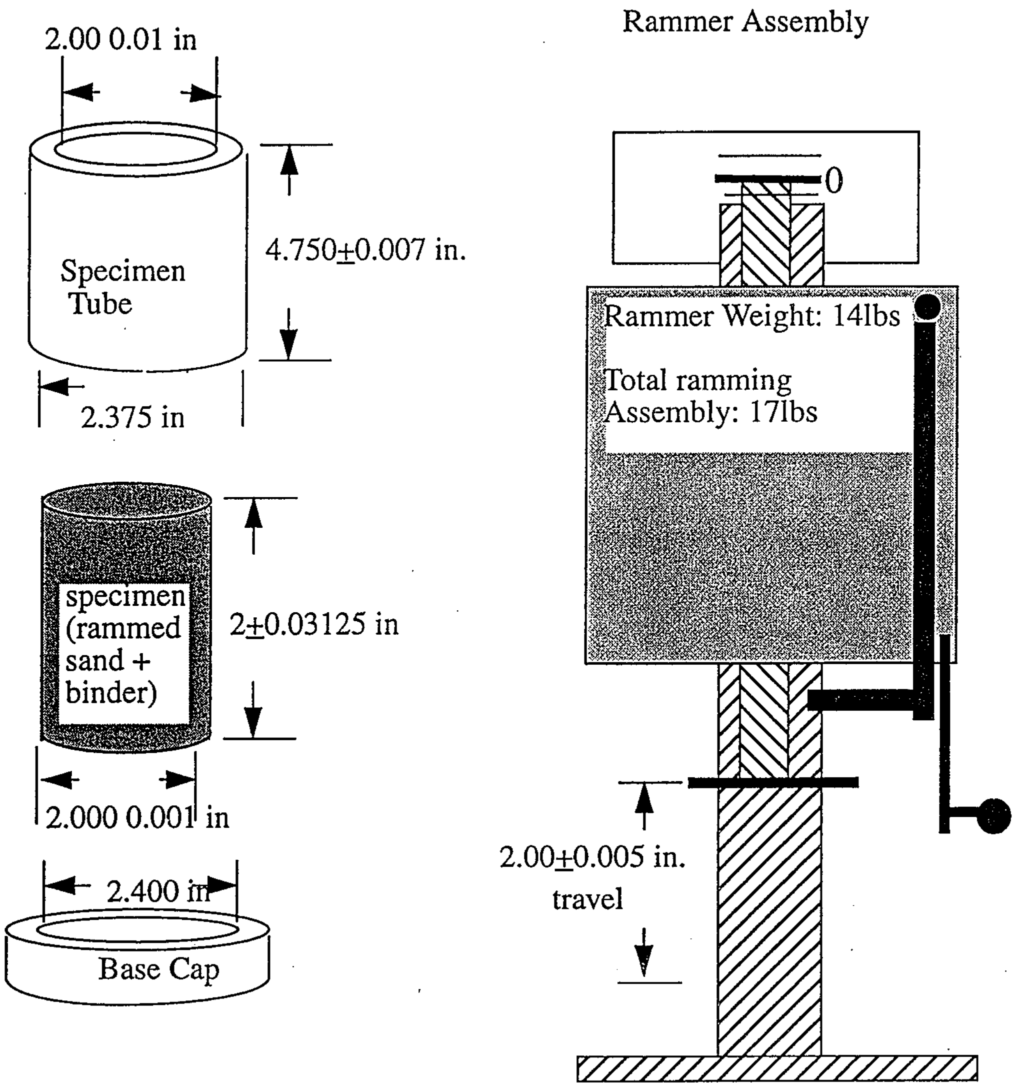


Figure 2. Sand ramming machine, used for making standardized cylinders of sand for compression, shear, and permeability testing.

Experiments were then conducted to determine the effects of varying the curing time of the samples on the compressive strengths and shear strengths of the samples. It was also noted that an exothermic chemical reaction was occurring between the fly-ash and the water, suggesting that the binding properties could be altered by initiating the fly-ash/ water reaction before adding the binder to the sand. Therefore, experiments were also carried out to determine the effects of varying the reaction initiation time.

Ultimately, the procedure was fixed at the best reaction initiation time (20 minutes) and curing time (1 hour). Experiments were conducted using both the ADM and Edwards fly-ashes. The water dosage was varied to determine the minimum amount needed to produce or exceed the target values for shear strength, compressive strength, and permeability. The carbon content of the Class F fly-ash was also varied by using varying ratios of high-

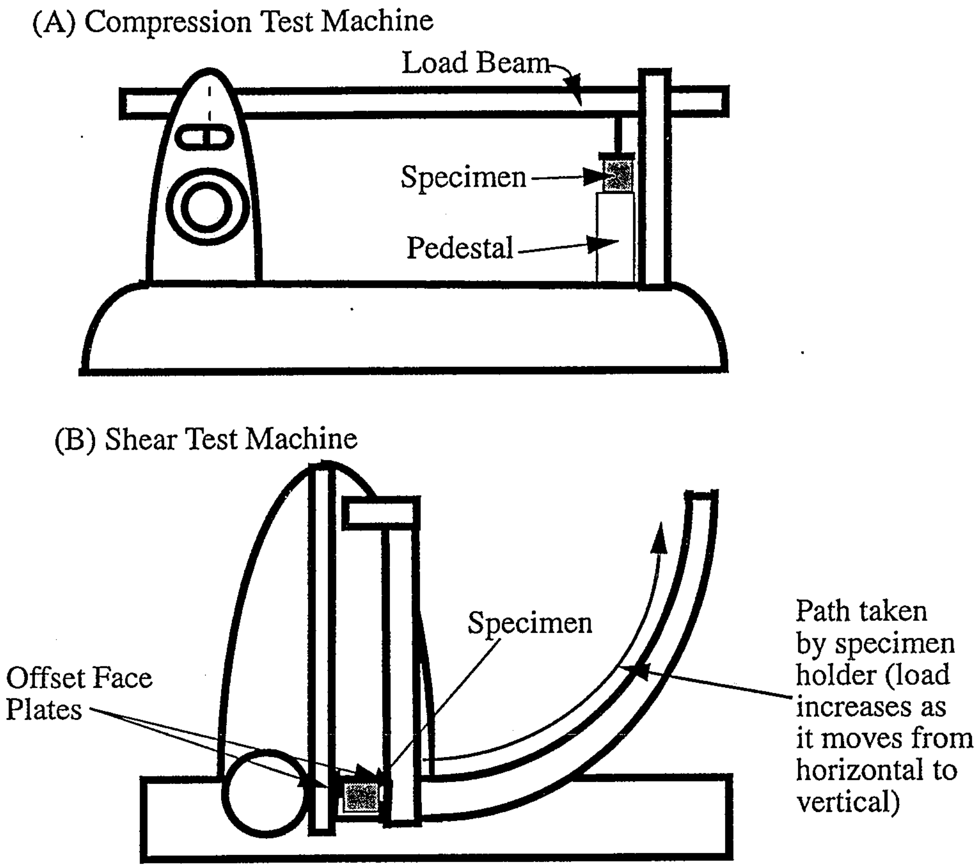


Figure 3. Schematics of the compression and shear machines used for measuring compression strengths and shear strengths of specimen cylinders.

carbon and lower-carbon ashes, to determine the effects of carbon content.

Experiments were also carried out to determine the temperature resistance of the fly-ash bonded specimens, and to compare their performance to that shown by bentonite binders. These experiments were conducted by pre-heating a muffle furnace to 600°C, and then placing cured sand specimens in the pre-heated furnace for 10 minutes. The specimens were then removed from the furnace, and cooled to room temperature for testing to determine whether the shear strengths or compressive strengths had changed.

RESULTS AND DISCUSSION

A series of factorially-designed experimental tests were run to determine what concentrations of fly-ash, $CaCl_2 \cdot 2H_2O$, and water would produce sand specimens that would most nearly able to meet the following target values:

- Compressive Strength greater than 15 psi.
- Permeability greater than 150 (AFS permeability number).
- Shear Strength greater than 4.5 psi.

These target values were established using standard bentonite binder. Of these initial tests,

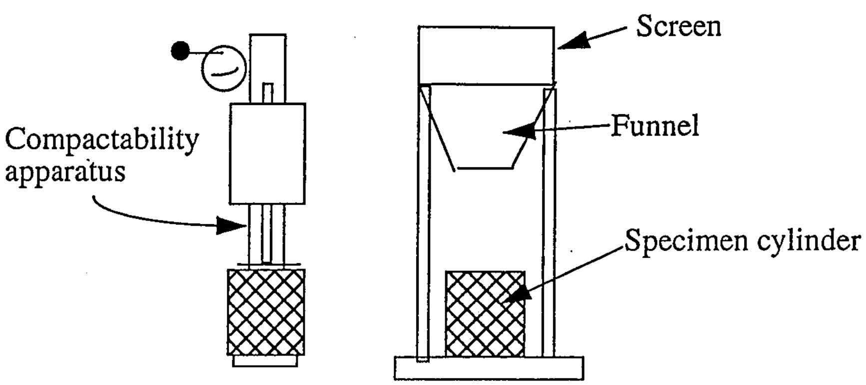


Figure 4. Compactability test apparatus. A test cylinder is loosely filled with a sand mixture that has been de-lumped through a 6.35 mm screen, and then compressed with a calibrated load. The compactability is then the percent change in height of the sand mixture.

only one produced results that were substantially better than the rest. The binder dosages for this particular test were:

- Fly-ash: ADM fly-ash, 9.67% of sand weight.
- $CaCl_2 \cdot 2H_2O$, 4.67% of sand weight.
- H_2O, 6.14% of sand weight.

Unfortunately, the values produced by this mixture using the original procedure were still substantially lower than that of the bentonite binder. Since the fly-ash and accelerator dosages were already quite high, it was decided that the most promising method for improving the properties of the bonded sand to meet the required targets was to alter the processing conditions.

From the results shown in Table 3, it can be seen that providing a curing time of 1 hour produced higher compressive and shear strengths compared to no curing time, and increasing the curing time to 3 hours increased the strengths further. Based on these results, the curing time for sand specimens was set at 1 hour.

Subsequent experiments varied the "reaction initiation time", which was the time allowed for fly-ash, water, and calcium chloride to begin to react before they were added to the sand. In these experiments, it appeared that the greatest strengths were reached with reaction initiation times of 20 minutes, as shown in Table 4. However, subsequent attempts to reproduce the 20 minute results showed that there was a great deal of variability from test to test when both reaction initiation time and curing time were allowed. Specimens which had low compressive and shear strengths were seen to be cracking during the curing phase. It is known that CaO expands as it hydrates to $Ca(OH)_2$, and it was believed that CaO in the fly-ash which had not completely hydrated during the mixing stage was expanding and causing cracking during the curing stage.

Table 2: Comparison between baseline results using Bentonite sand, and results from Fly-ash testing using factorial experiments

Test	Sand lbs (wt%)	Bentonite Clay lbs (wt%)	Fly Ash lbs (wt%)	CaCl$_2$ lbs (wt%)	H$_2$0 lbs (wt%)	Measured H$_2$0 wt% of sample	Compressive Strength psi	Permeability AFS#	Compactibility % decrease in total height	Shear Strength psi
Base line	10.00 (92.81)	0.60 (5.57)	0.0 (0.0)	0.0 (0.0)	0.175 (1.62)	2.3 ±0.3	15.0 ±0.6	154.7 ±5.0	51.0 ±1.7	4.5 ±0.1
1	14.00 (82.28)	0.0 (0.0)	1.35 (8.03)	0.65 (3.87)	0.81 (4.81)	5.1 ±0.2	3.9 ±0.3	106.7 ±15.3	44.67 ±0.6	1.2 ±0.1
2	13.50 (85.38)	0.0 (0.0)	1.35 (8.54)	0.15 (1.04)	0.81 (5.12)	4.9 ±0.4	1.7 ±0.1	79.0 ±5.3	40.7 ±0.6	1.4 ±0.0
3	13.60 (86.57)	0.0 (0.0)	0.65 (4.14)	0.65 (4.14)	0.81 (5.16)	5.9 ±0.3	1.6 ±0.0	62.3 ±4.6	40.3 ±0.6	1.2 ±0.0
4	13.25 (89.17)	0.0 (0.0)	0.65 (4.37)	0.15 (1.01)	0.81 (5.45)	5.7 ±1.0	1.2 ±0.0	76.7 ±10.4	37.7 ±0.6	1.3 ±0.1
5	13.65 (85.15)	0.0 (0.0)	1.33 (8.30)	0.65 (4.05)	0.40 (2.43)	3.1 ±0.2	2.4 ±0.3	148.3 ±16.1	36.3 ±2.9	1.2 ±0.2
6	13.65 (88.64)	0.0 (0.0)	0.65 (4.22)	0.7 (4.55)	0.40 (2.60)	3.9 ±0.3	1.5 ±0.1	100.7 ±1.2	41.0 ±1.0	1.2 ±0.1
7	13.65 (86.50)	0.0 (0.0)	0.65 (4.12)	0.67 (4.25)	0.81 (5.09)	4.9 ±0.1	1.2 ±0.0	91.7 ±2.9	36.0 ±0.0	1.1 ±0.1

% Compactibility = loss of height at 140 psi applied pressure, divided by total height of loose mass

AFS Permeability # = $\frac{v \bullet h}{p \bullet a \bullet t}$ where v= volume of air passing through sample, cm^3; h = height of sample, cm;

p = pressure head, 10 cm H$_2$0 (10 g/cm^2); a = cross-sectional area of sample, cm^2; t = time, seconds

Table 3: Mean permeability, compressive strengths, and shear strengths at different $CaCl_2 \cdot 2H_2O$ dosage levels and different curing times, with standard deviations and 95% tolerance. All samples contain 10.0% ADM fly-ash and 6.0% H_2O. All percentages are by weight of sand (sand weight = 100%). Permeabilities were only measured before curing, because the measurement must be made before the sand specimen is removed from the molding cylinder to cure.

$\%CaCl_2 \cdot 2H_2O$ added		1.0	5.0		
Curing time of samples		1 hr	0 hr	1 hr	3 hr
# of replications		3	3	6	6
Permeability (AFS number)	Mean	91.7	106.7		
	Std. Deviation	1.2	15.28		
	P_{95}	+/-2.0	+/-25.5		
Compressive Strength (psi)	Mean	6.3	3.87	16.1	22.0
	Std. Deviation	0.5	0.3	2.0	2.7
	P_{95}	+/-0.8	+/-0.5	+/-1.65	+/-2.2
Shear Strength (psi)	Mean	2.2	1.23	4.52	7.10
	Std. Deviation	0.10	0.12	0.2	1.2
	P_{95}	+/-0.20	+/-0.2	+/-0.2	+/-1.0

Table 4: The mean permeabilities, compressive strengths, and shear strengths of test samples at various reaction initiation times with standard deviations and 95% tolerances. All samples contain 10.0% ADM fly-ash, 3.0% $CaCl_2 \cdot 2H_2O$, and 6.0% H_2O. All percentages are by weight of sand (sand weight = 100%).

Reaction Initiation Time		10 min	20 min		1 hour	
Curing time of samples		1 hr	0 hr	1 hr	0 hr	1 hr
# of replications		3	12	15	3	3
Permeability (AFS number)	Mean	147.3	147.9		148.3	
	Std. Deviation	14.2	33.9		2.89	
	P_{95}	+/-23.9	+/-15.4		+/-4.87	
Compressive Strength (psi)	Mean	8.5	3.8	13.8	3.5	6.1
	Std. Deviation	1.0	0.4	9.8	0.5	1.0
	P_{95}	+/-1.7	+/-0.2	+/-1.8	+/-0.8	+/-1.7
Shear Strength (psi)	Mean	2.6	1.1	5.0	1.4	2.3
	Std. Deviation	0.3	0.2	4.0	0.2	1.3
	P_{95}	+/-0.5	+/-0.1	+/-1.8	+/-0.3	+/-2.2

To ensure that the CaO in the fly-ash was hydrating fully, an insulated reaction vessel was used for the initial reaction of the fly-ash with the water and calcium chloride. Measurement of the temperature of the fly-ash/water/calcium chloride mixture in this vessel showed that it rapidly heated to near the boiling point of water, and held this temperature for several minutes before beginning to decrease again by the end of the 20 minute period, as shown in Figure 5. This decrease in temperature indicated that the hydration of the fly-ash was complete, and no cracking of the samples was observed in cured specimens after this method of reaction initiation was adopted.

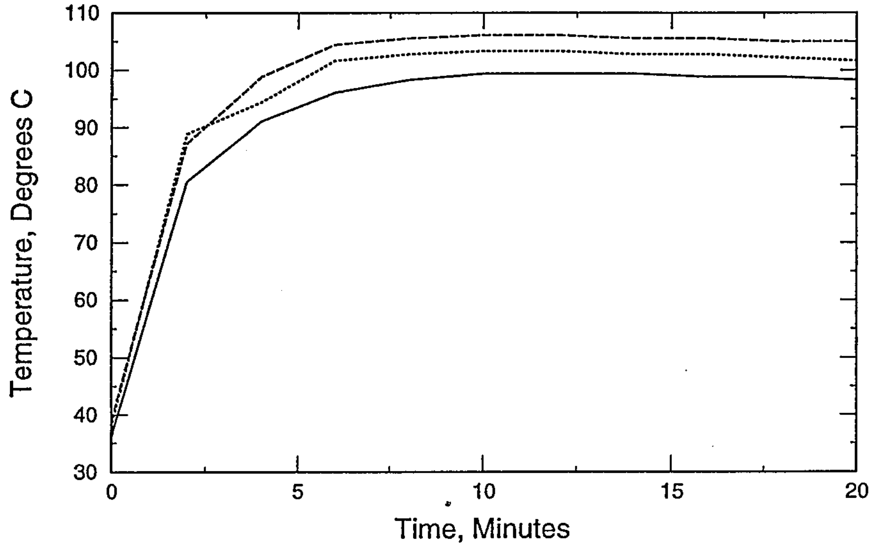


Figure 5. Temperature profiles for hydration of ADM fly-ash in an insulated vessel.

From the experimental tests that were conducted using ADM fly-ash, the following trends were observed:

- Compressive strengths and shear strengths increased when the fly-ash slurry was allowed to fully hydrate.
- When allowed to cure for one hour, the compressive strengths and shear strengths met and exceeded the target values set by the bentonite binder.

Based on the preceding results, the first alteration made to the process was to introduce a curing time interval, after it was noted that sand specimens became stronger upon curing in air. This resulted in higher compressive and shear strengths compared to no curing time. Based on these results, the curing time for sand specimens was set at 1 hour.

From the experimental tests that were conducted using ADM fly-ash, the following trends were observed:

- Compressive strengths and shear strengths increased when the fly-ash slurry was allowed to fully hydrate.
- When allowed to cure for one hour, the compressive strengths and shear strengths met and exceeded the target values set by the bentonite binder.

In early experiments using the Edwards ash, the following observations were made:

- The compressive strengths and shear strengths of the sample using the Edwards ash without supplementary calcium oxide or hydroxide were drastically reduced compared to samples using ADM ash at the same dosage.
- Sample compressive strengths and shear strengths exceeded those of ADM fly-ash when CaO was added to the fly-ash to raise the calcium percentage to that of the ADM fly-ash; however, the permeability of the sample was lowered considerably.
- When $Ca(OH)_2$ was added to the fly-ash in amounts comparable to those that would be produced by H_2O reacting with CaO, the compressive strengths and shear strengths again exceed those of the ADM fly-ash, but again the permeability was considerably lower than that of the bentonite binder.

Table 5: Properties of Specimens made with 10.00% ADM fly-ash, 5.00 % $CaCl_2$, and 6.00% water at different curing times. Percentages are by weight of sand

Binder Material	Cure Time (hr)	Permeability	Compressive strength (psi)	Shear strength (psi)
Bentonite Clay	0	182.7±10.2	14.1±1.7	5.0±0.6
Fly-ash	0	106.7±15.3	3.9±0.3	1.2±0.1
Fly-ash	1	107.7±2.5	16.9±0.9	4.6±0.2
Fly-ash	3	113.3±5.8	22.8±3.1	8.0±0.3

Table 6: Properties of Specimens made with 10.00% ADM fly-ash, 3.00 % $CaCl_2$, and 6.00% water curing for 1 hour at different reaction initiation (R.I.) times. Percentages are by weight of sand

Binder Material	R.I. Time (min)	Permeability	Compressive strength (psi)	Shear strength (psi)
Bentonite Clay	0	182.7±10.2	14.1±1.7	5.0±0.6
Fly-ash	0	142.7±15.5	3.6±0.4	1.3±0.1
Fly-ash	10	147.3±14.2	8.5±1.0	2.6±0.3
Fly-ash	20	132.3±2.5	30.3±6.3	12.1±0.5
Fly-ash	60	148.3±2.9	6.1±1.0	2.3±1.3

In both Table 5 and Table 6, the bentonite binder was used without either a reaction initiation time or a curing time. The effectiveness of the ADM fly-ash binder improved when the fly-ash, calcium chloride, and water were combined and allowed to react (reaction initiation) before combining with the sand. The best results were obtained with a

20 minute reaction initiation time. With both a 20 minute reaction initiation time, and a 1 hour curing time, sand specimen properties were comparable to those obtained with conventional bentonite binder, as shown in Table 7.

Table 7: Properties of Specimens made with 10.00% ADM fly-ash, 3.00 % $CaCl_2$, and 6.00% water. Curing was for 1 hour with a 20 min reaction initiation time. Percentages are by weight of sand

Binder Material	Permeability	Compressive strength (psi)	Shear strength (psi)
Bentonite Clay	182.7±10.2	14.1±1.7	5.0±0.6
ADM fly-ash	168.3±15.7	22.9±6.9	7.4±2.2

Effects of Moisture Content

Experiments were conducted to determine the effects of variations in moisture content on the sand specimen properties, using each of the different fly-ashes. The fly-ashes tested were the ADM fluid-bed combustor ash, and a sample of fly-ash from the E. D. Edwards plant with a carbon content of 6.87% ("Edwards Low-Carbon Fly-Ash"). The binder compositions used in these experiments were as follows (all percentages given as percent of the sand weight):

- ADM ash: Fly-ash dosage 10% of the sand weight, with 3% calcium chloride
- Edwards Low-Carbon ash, with CaO: Fly-ash dosage 6% of the sand weight, with 4% CaO and 3% calcium chloride
- Edwards Low-Carbon ash, with $Ca(OH)_2$: Fly-ash dosage 6% of the sand weight, with 5.28% $Ca(OH)_2$ and 3% calcium chloride

In these experiments, the moisture content was varied by altering the amount of water added along with the binder. The fly-ash results were compared to the baseline results obtained earlier using bentonite binder added at a dosage of 6% of the sand weight, with 2% moisture.

Permeability was found to be a strong function of the moisture content, with the highest permeability achieved at a moisture content of approximately 3.5% for the ADM ash, and at 4% for the Edwards ash, as can be seen from Figure 6. The ADM ash reached a maximum permeability that was comparable to that of the bentonite binder, while the permeabilities for the Edwards ash were significantly lower.

Increasing water addition also increased the compressive strength, as shown in Figure 7 and Figure 8. The compressive strength with no curing time (Figure 7) reached its maximum value at 4% moisture for the ADM ash and the Edwards ash with calcium hydroxide, and at nearly 5% moisture for the Edwards ash with calcium oxide. Before curing, the Edwards ash with calcium oxide showed a higher strength that the Edwards ash with calcium hydroxide, indicating that calcium oxide is a better choice for a calcium

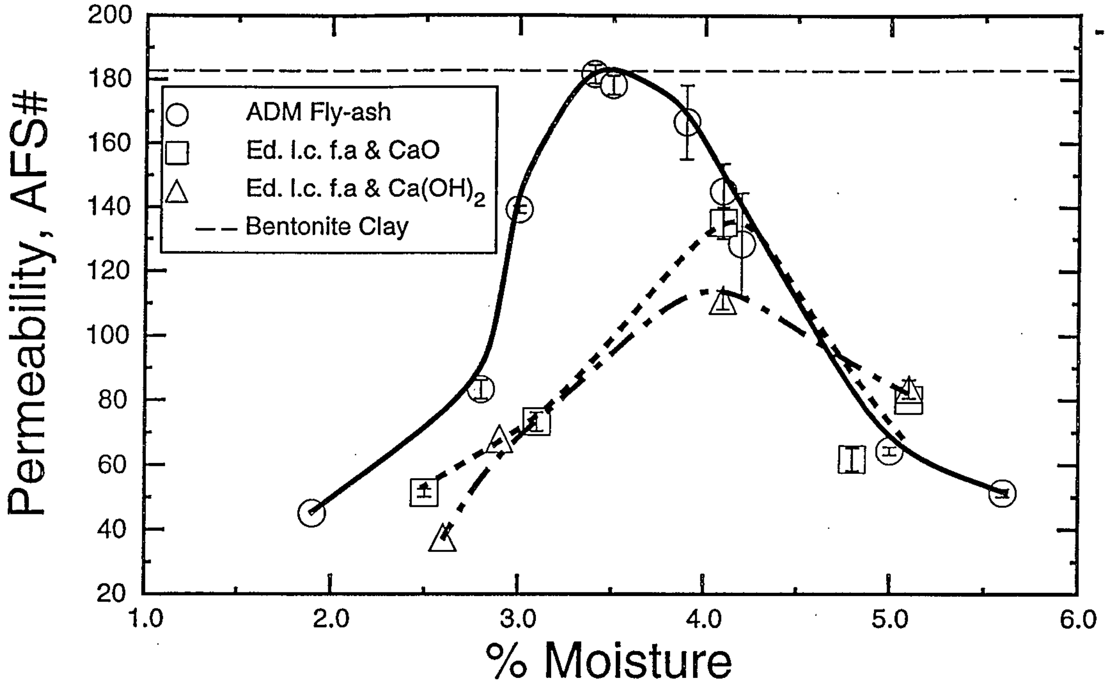


Figure 6. AFS permeability number as a function of moisture content for AFS standard sand specimens using ADM and Edwards low-carbon fly-ashes as binder. The dashed line is the baseline permeability obtained with bentonite binder at 2% moisture.

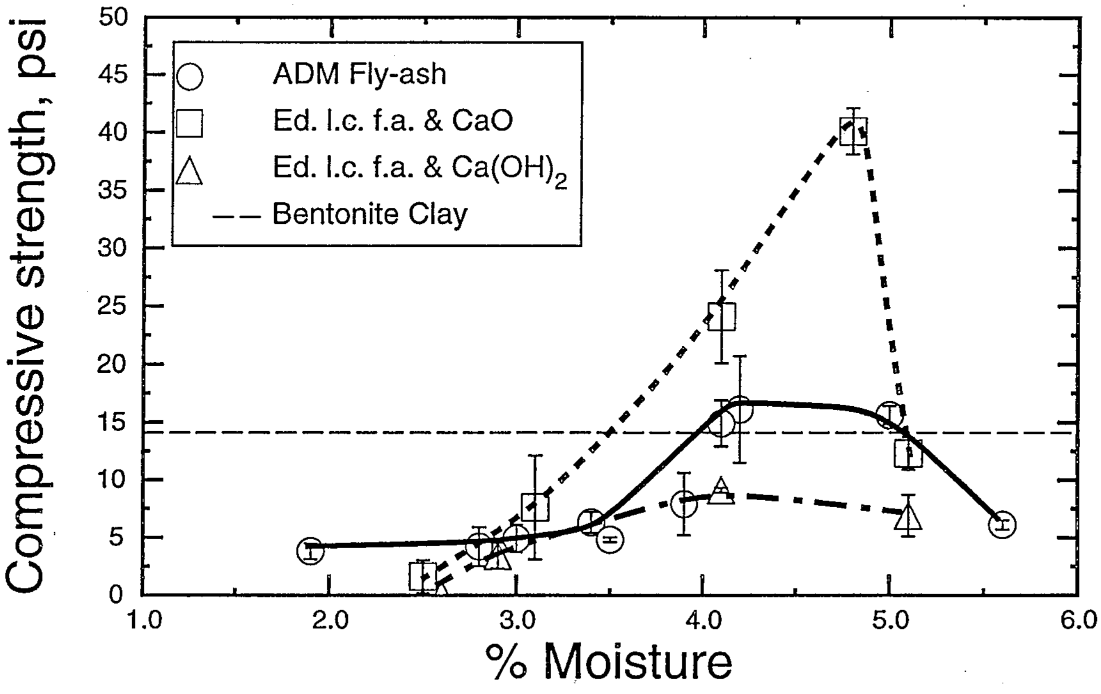


Figure 7. Effect of moisture content on the compressive strength of AFS standard sand specimens using ADM and Edwards low-carbon fly-ash binders, before curing. The dashed line is the baseline permeability obtained with bentonite binder at 2% moisture.

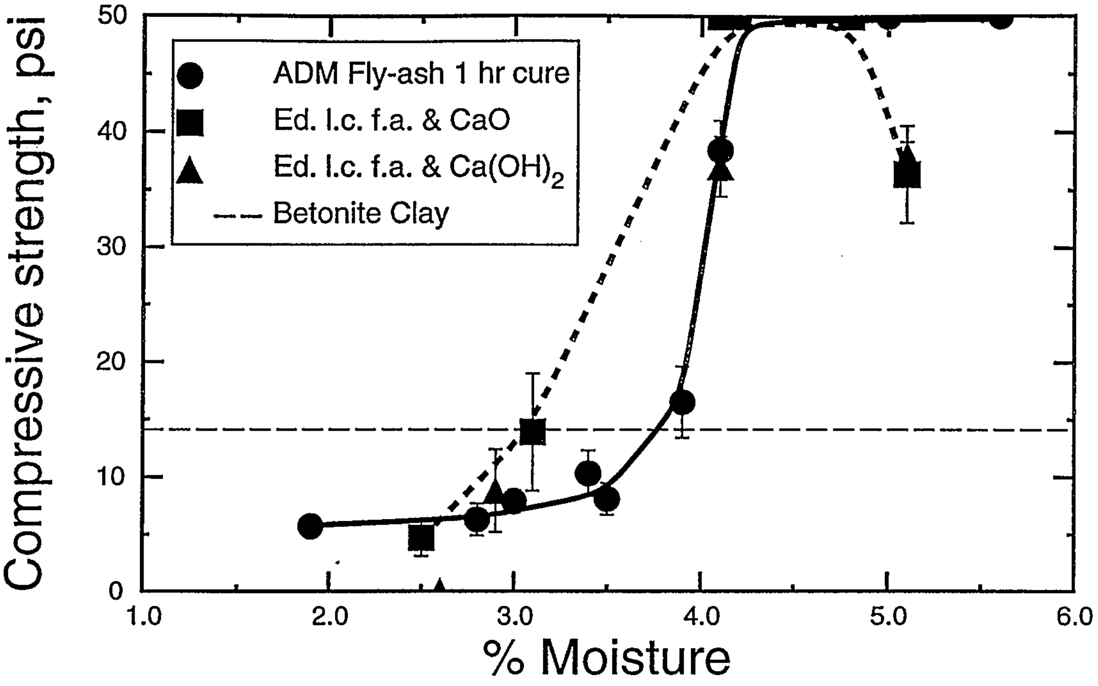
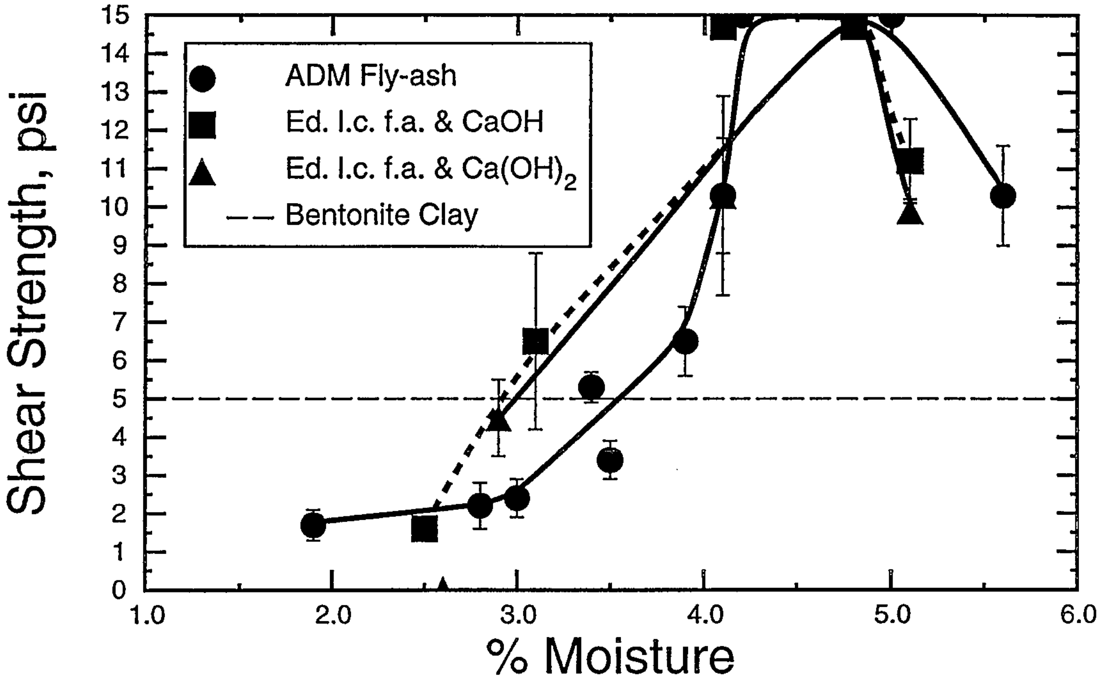


Figure 8. Effect of moisture content on the compressive strength of AFS standard sand specimens using ADM and Edwards low-carbon fly-ash binders, after curing for 1 hour. The dashed line is the baseline permeability obtained with bentonite binder at 2% moisture.



igure 9. Effects of moisture content on shear strength for AFS standard sand specimens using ADM and Edwards low-carbon fly-ash binders, after curing for 1 hour. The dashed line is the baseline permeability obtained with bentonite binder at 2% moisture.

source than calcium hydroxide. After providing a 1 hour curing time (Figure 8), the compressive strengths increased for all of the binders tested, which all equalled or exceeded 50 psi when they had moisture contents in the range from 4% to 4.5% moisture.

Shear strength of the test specimens was too low to be reliably measured for all of the fly-ash bonded specimens when no curing time was provided. However, when a 1 hour curing time was used, the shear strength increased, and measurements produced the results shown in Figure 9. At moisture contents greater than about 3.0 - 3.5%, the cured shear strength was higher than the shear strengths obtained with bentonite binder.

Temperature Resistance

In the temperature-resistance experiments, it was found that the compressive and shear strength for bentonite-bonded sand after heating to 600°C were similar to the values before heating, as can be seen from Table 8. Similarly, the sand bonded with ADM ash remained at approximately the same strength after firing as before firing. There was some concern that the fly-ash binder would begin to melt, which would be undesirable because melted sand/binder mixture would be difficult to remove from a finished casting. However, examination of the specimens showed no evidence of melting or sintering of the sand/binder mixture at this temperature for either the bentonite-bonded sand or the fly-ash bonded sand.

Table 8: Comparison of the effects of heating sand specimens to 600°C for 10 minutes, for both bentonite-bonded sand, and ADM fly-ash-bonded sand. The bentonite was added at a dosage of 6% of the sand weight. The ADM fly-ash was added at a dosage of 10% of the sand weight, along with calcium chloride at 3% of the sand weight as a curing accelerator, and was cured for 1 hour before heating. The "green" strengths are before heating, and the "fired" strengths are after heating.

Binder	% Moisture	Compression Strength (psi)		Shear Strength (psi)	
		Green	Fired	Green	Fired
Bentonite	2.0	14.1 +/- 0.1	16.1 +/- 1.1	5.1 +/- 0.2	4.4 +/- 0.9
ADM Fly-Ash	4.2	28.9 +/- 6.0	21.4 +/- 1.7	9.9 +/- 1.0	6.3 +/-2.2

Specimens made with High and Low Carbon Edwards fly-ashes either crumbled or developed cracks upon removal from the muffle furnace or did not register a compressive or shear strength when tested.

At higher temperature (1000°C), specimens made from bentonite did not crumble upon removal from muffle furnace but, upon cooling the specimens crumbled and could not be tested for compressive and shear strength. Specimens that were made with High or Low Carbon fly-ash and fired at 1000°C either exhibited cracks and crumbled upon removal from muffle furnace or developed cracks upon removal and crumbled later due to minor disturbances. The samples bonded with ADM fly-ash performed similarly to the bentonite-bonded specimens at this temperature.

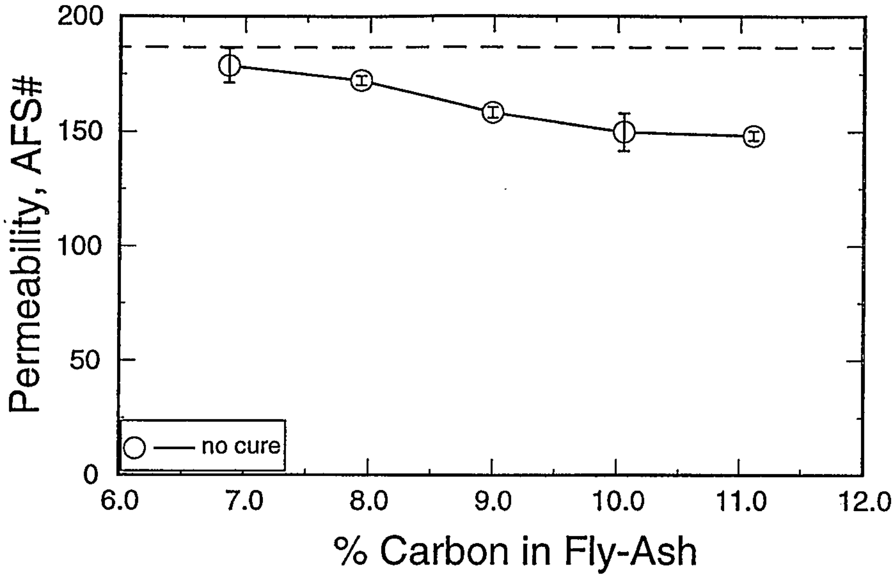


Figure 10. Permeability of sand specimens when bonded with Class F fly-ashes of varying unburned carbon contents. The dashed line represents the target value obtained with bentonite binder at 2% moisture.

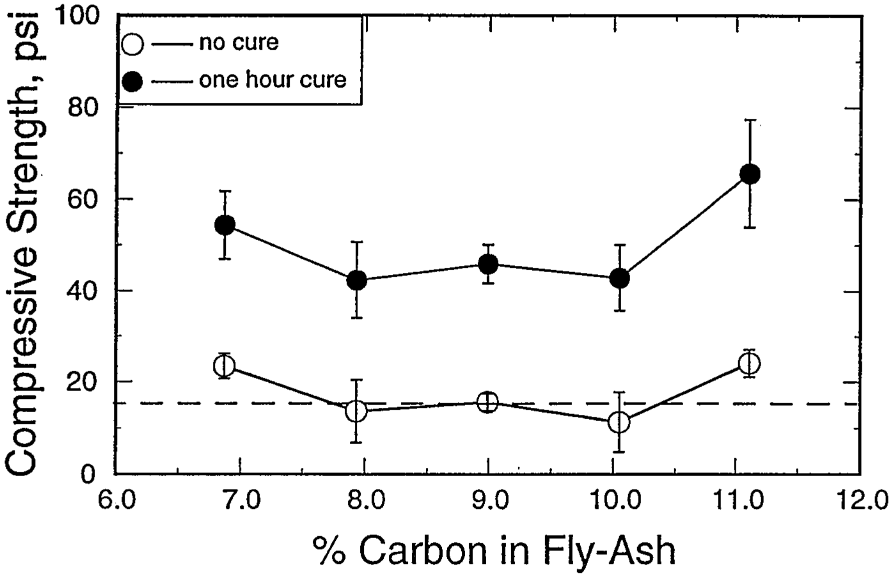


Figure 11. Compressive strengths of foundry sand specimens when bonded with Class F fly-ashes of varying carbon contents. The dashed line represents the target value obtained with bentonite binder at 2% moisture.

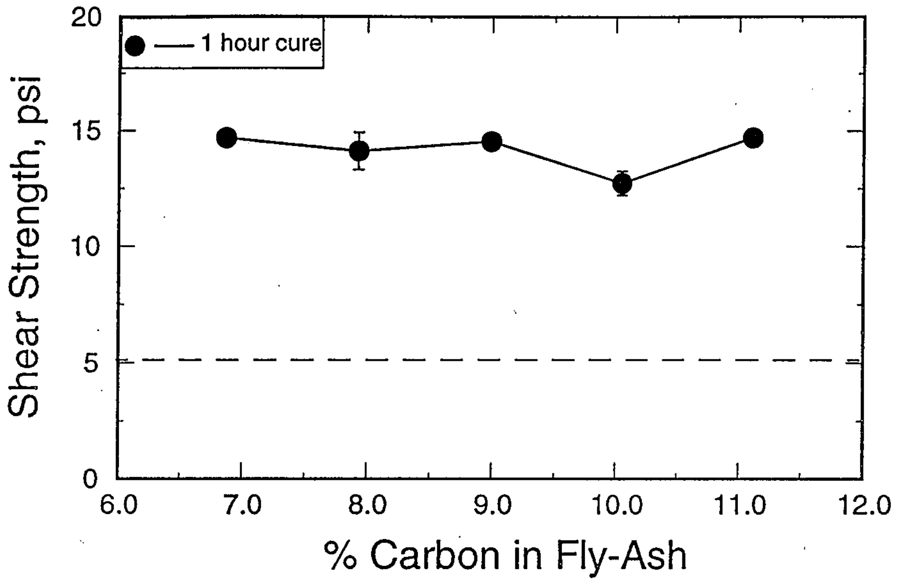


Figure 12. Shear strengths of foundry sand specimens when bonded with Class F fly-ashes of varying carbon contents. The dashed line represents the target value obtained with bentonite binder at 2% moisture.

Carbon Content Studies

Carbon content was varied by using various proportions of the Edwards high-carbon and low-carbon fly-ashes. Since these ashes were chemically similar aside from their carbon contents, these experiments were used to determine whether carbon content had any significant effects on the properties of the bonded sand.

In general, the carbon content did not have a regular, systematic effect on the sand properties, as shown by Figure 10, Figure 11, and Figure 12. These results imply that the carbon content would not have any harmful effect on the use of fly-ashes as foundry-sand binder.

Recyclability Studies

Since foundry sands are used repeatedly in actual industrial practice, studies were conducted to determine whether the material could be recycled after it has been bonded, cured, and broken up again. The recycle procedure used is shown schematically in Figure 13. The sand recycled satisfactorily provided that additional binder was added, and so there are no serious obstacles to recycling fly-ash-bonded foundry sand.

CONCLUSIONS AND RECOMMENDATIONS

From the studies completed in this project, the following conclusions were reached:

1. Fly-ash binders require moisture contents of 3.5 - 4.0% for the best permeability, and 4.0 - 5.0% for the best compressive and shear strengths. The ADM fly-ash can reach a higher permeability value than the Edwards ash at a comparable dosage, but the compressive and shear strengths are similar for both ashes.

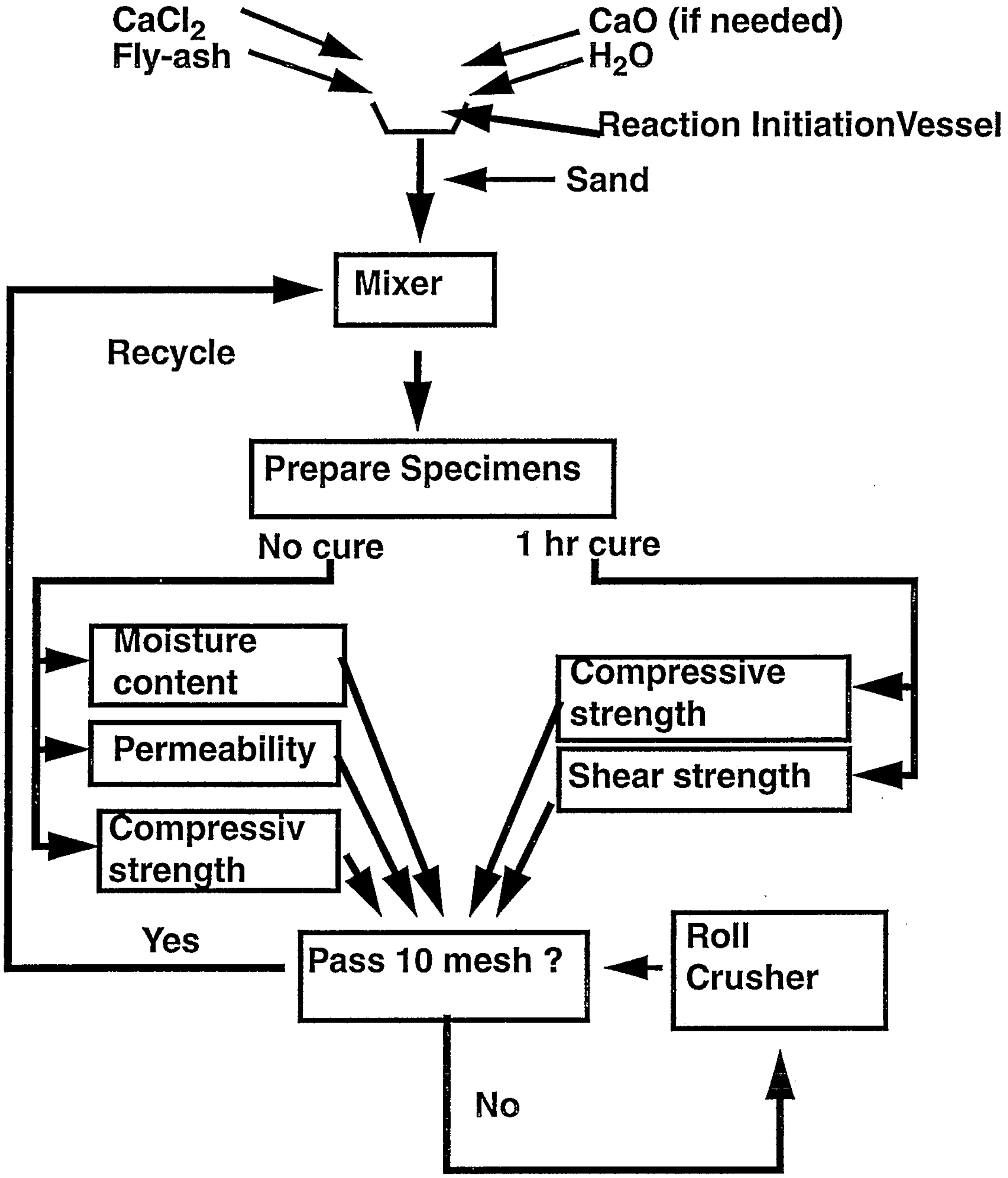


Figure 13. Testing procedure used, showing recycle procedure for sand specimens.
Fresh binder was added to the recycled sand as needed.

2. The Edwards ash requires supplemental calcium, in the form of either calcium oxide or calcium hydroxide, before it can function as a binder. When calcium hydroxide is used, the strength before curing is lower than the uncured strength using calcium oxide, although results are comparable after curing. Of the two types of supplemental calcium, the calcium oxide appears to give the best results.
3. The ADM ash has acceptable temperature-resistance properties up to a temperature of at least 600°C. Further experimentation is needed at higher temperatures, and also to determine the temperature resistance of the Edwards ashes.
4. Unburned carbon in the fly-ash does not have any obvious harmful effects on the properties of the bonded foundry sands. This application is therefore well-suited for use of the high-carbon ashes that cannot be utilized by other fly-ash applications.

The necessary conditions have been determined for using a range of fly-ashes as binders for foundry sands. With the proper processing and handling, the ash binders can bind the foundry sand as effectively as the higher-cost bentonite binders. The use of these binders to bond foundry sands in industrial applications is therefore very promising, and it will only be necessary to conduct actual metal-casting experiments to demonstrate the value of this technology to the foundry industry.

DISCLAIMER STATEMENT

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PROJECT MANAGEMENT REPORT
June 1, 1997, through August 31, 1997

Project Title: **USE OF FLY-ASH-BASED BINDERS FOR FOUNDRY MOLDS**

ICCI Project Number:	96-1/3.1A-1
Principal Investigator:	S.K. Kawatra, Department of Metallurgical and Materials Engineering, Michigan Technological University
Other Investigators:	T. C. Eisele, Department of Metallurgical and Materials Engineering, Michigan Technological University N.W. Burrows, Department of Metallurgical and Materials Engineering, Michigan Technological University
Project Manager:	D. Banerjee, ICCI

COMMENTS

The project is proceeding according to the proposed schedule.

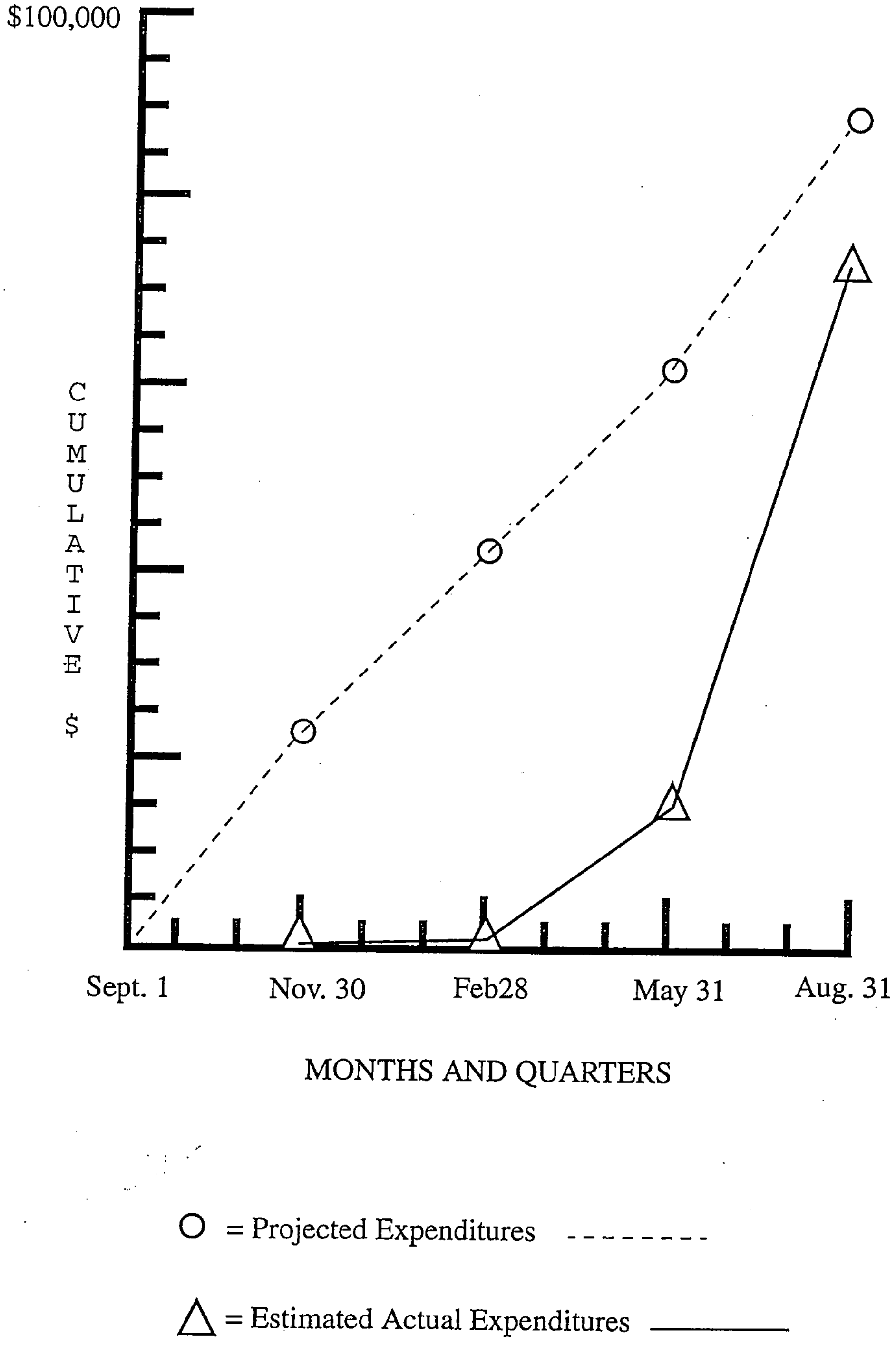
Projected and Estimated Expenditures

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1996 to Nov. 30, 1996	Projected	10,079	2,245	500	1,500	0	901	6,850	22,075
	Estimated	0	0	0	0	0	0	0	0
Sept. 1, 1996 to Feb. 28, 1997	Projected	20,158	4,491	1,000	1,500	0	1,819	13,700	42,668
	Estimated	0	0	65	0	0	0	30	95
Sept. 1, 1996 to May 31, 1997	Projected	30,237	6,736	1,500	1,500	0	2,729	20,550	63,252
	Estimated	9,710	3,398	1,010	0	0	130	536	16,460
Sept. 1, 1996 to Aug. 31, 1997	Projected	40,316	8,981	6,000	3,000	0	3,638	27,400	89,335
	Estimated	32,210	8,881	8,629	417	0	698	23,562	74,397

*Cumulative by Quarter

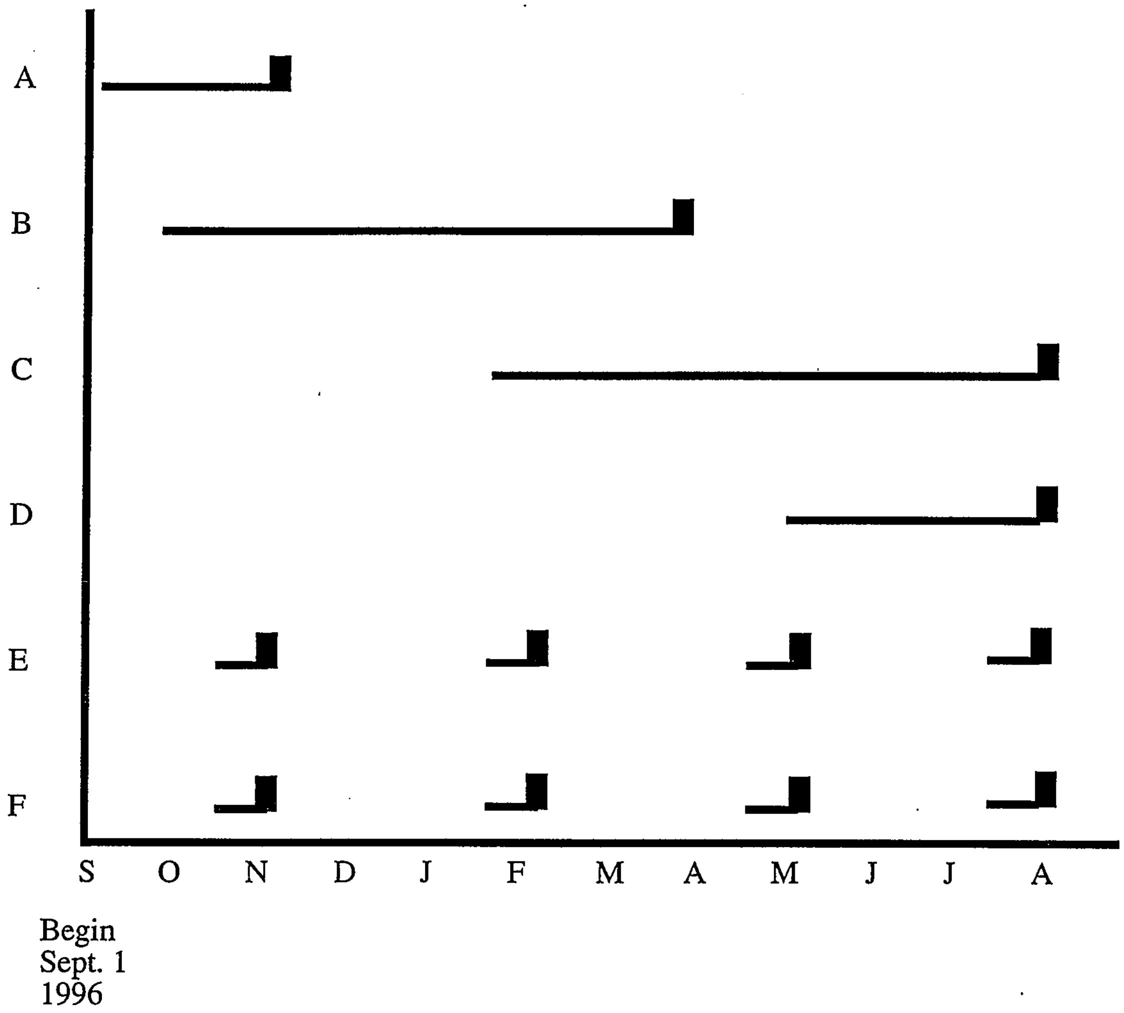
COSTS BY QUARTER

"Use of Fly-Ash-Based Binders for Foundry Molds"



Total Illinois Clean Coal Institute Award: $89,335

SCHEDULE OF PROJECT MILESTONES



Milestones

A. Task 1: Sample Preparation and Experimental Design
B. Task 2: Binder Strength Determination
C. Task 3: Binder Temperature Resistance Determination
D. Task 4: Binder Recyclability Determination
E. Technical Reports Prepared and Submitted
F. Project Management Reports Prepared and Submitted