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COMPARISON OF CLASS C AND CLASS F FLY-ASHES AS FOUNDARY SAND BINDERS AND THE EFFECTIVENESS OF ACCELERATORS IN REDUCING CURING TIME

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Fly-ashes are a potential alternative to conventional bentonite to be used as binders for the production of foundry sand molds. The performance of two different fly-ashes in this application was evaluated. These fly-ashes were classified as a Class F (pozzolanic) ash and a Class C (pozzolanic and cementitious) ash according to American Society for Testing and Materials (ASTM) specifications. It was determined that both types of fly-ash could reach bonding strengths in the test specimens that were higher than that achieved with bentonite. However, the Class C ash required less than one-tenth as much curing time as the Class F ash to reach strengths comparable to those of bentonite-bonded specimens. It was also determined that the use of accelerators allowed the necessary curing time of Class C ash to be reduced to less than an hour.

Keywords: fly-ash, binder, bentonite, foundry sand, pozzolanic, accelerator

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In foundry mold production, a binder is needed to achieve the desired physical properties for the sand mold. The most common binder in current practice is bentonite clay, which binds sand grains together such that the sand/binder/water mixture develops the necessary compressive strength, shear strength, and compactability. Foundries are major consumers of bentonite clay; it is estimated that 801,750 metric tons of bentonite were consumed by U.S. foundries in 2001 (U. S. G. S 2002a). The cost of bentonite is around $60 per metric ton and as much as two-thirds of the final cost is from shipping, because most foundries are located far from the bentonite production plants. Furthermore, bentonite is a nonrenewable resource that is gradually being depleted; therefore, a low-cost alternative is desirable.

Fly-ash is a by-product of coal-fired electricity generation plants. It consists of fine pozzolanic particles collected from coal combustion exhaust gases. An estimated 57.1 million metric tons of fly-ash were produced in the U.S. in 2000 (USGS 2002b). Only an estimated 30.9% of this fly-ash was utilized, with the remainder disposed of in landfills. As a result, fly-ash is highly available for little more than the cost of shipping and, since power plants are located relatively close to the population centers that support foundries, the cost of shipping fly-ash will be less than the cost of shipping bentonite from distant deposits.

Two factors encourage the use of fly-ash as a foundry mold binder. One is lower materials and shipping cost and the other is that, under the correct conditions, fly-ash can have binding properties comparable to those of bentonite.

THEORETICAL BACKGROUND

While the chemical compositions of fly-ashes are similar to bentonites, the mechanisms of binding are completely different. Bentonite produces a physical bond between sand grains, while fly-ash undergoes a chemical reaction with water to produce the bond.

Binding Mechanisms of Fly-Ash

Fly-ash is primarily fine particles of aluminosilicate glass produced by melting of the mineral phases present in coal during combustion (ASTM C618-98 1998). When these glassy particles contact water and calcium
hydroxide, they react to form an amorphous calcium aluminosilicate hydrate gel, which cements particles such as sand grains together. This is defined as a pozzolanic reaction and gives the sand mixture compactability, permeability, and strength. Unlike the rapid physical bonding of bentonite, basic fly-ash-based binder (FBB) can take several hours or days to develop full strength.

The pozzolanic reaction is similar to the hardening of cement and, as a result it reacts to the same types of hardening accelerators and retarders that are used in Portland cement applications. In particular, salts such as calcium chloride and calcium nitrate can be used to increase the hardening rate (Taylor 1990).

Calcium chloride is the most widely studied and used cement hardening accelerator, having been in common use in cement and concrete for over 100 years, although the effects of other calcium–salt accelerators use similar principles (Forsen 1938; Platzmann 1926; Taylor 1990). The hardening of cement is the result of continuous calcium silicate dissolution resulting in precipitation of the gluing agent dicalcium silicate hydrate. As calcium chloride exothermically dissolves, hydration reactions are accelerated both by increased temperature and by the increased lime solubility in the calcium chloride solutions, which has a lower pH than pure water (Platzmann 1926); the lower pH also results in accelerated dissolution of the calcium silicates. The increased calcium ion concentration available from the calcium chloride and dissolved calcium hydroxide makes it possible for hydrates to precipitate and grow more rapidly (Forsen 1938). Finally, the calcium chloride retains water throughout the reaction, allowing the reaction to continue for longer by retarding evaporation that would otherwise be caused by the heat of reaction or by external heat sources during drying. Calcium chloride addition also retards the hydration of tricalcium aluminates while it accelerates the formation of tricalcium silicates and dicalcium silicates, and tends to keep the hydrated material in an amorphous or finely crystalline condition (Sloane et al. 1931). Furthermore, calcium chloride increases the calcium oxide/silicon dioxide (CaO/SiO₂) ratio of the calcium–silicate–hydrate (C–S–H) phase (Odler and Abdul-Maula 1987).

The major drawback of using calcium chloride as an additive for accelerating cement and pozzolanic reactions is that it also promotes corrosion of iron and other metals. To avoid corrosion problems, calcium nitrate can be used instead, which is nearly as effective of an accelerator as calcium chloride (Taylor 1990), but is much less corrosive.
Types of Fly-Ash

ASTM classifies marketable fly ashes as either Class F or Class C, which have the following characteristics (ASTM C618-98 1998).

- Class F fly ash is produced from burning anthracite or bituminous coal. It will react with calcium hydroxide and water to form cementitious compounds (known as a pozzolanic reaction). However, it does not show cementing behavior over short timescales if water is added without lime or other alkalies.

- Class C fly ash is produced from burning lignite or subbituminous coal. In addition to pozzolanic properties, it also exhibits strong cementitious properties with no additives other than water, because of a high free-lime content. Some Class C fly ashes contain more than 10% CaO as free lime.

For both types of fly ash, ASTM has set a maximum limit of 6% loss on ignition (LOI), which is a direct measure of unburned carbon content in fly-ash. Higher carbon contents are considered unacceptable for industrial use. Much of the fly-ash produced, particularly fly-ash from the low NOx burners that are currently being installed in many plants, contains more than 6% unburned carbon, which make it unusable for the conventional applications that have been developed for this material (Behr-Andres 1991).

EXPERIMENTAL

The experiments described in this article were carried out to compare the rates of strength development for Class F fly-ashes and Class C fly-ashes, with and without accelerator, and to determine whether they can be used to develop sufficient mold strength with curing times of less than a few hours.

Materials

The silica sand was obtained from Badger Mining Corporation, Berlin, WA, USA, and had an American Foundry Society (AFS) grain fineness number of 58.3. Its size distribution is shown in Table 1.

The fly-ashes used were a Class F type and a Class C type obtained from power plants in Wisconsin and Illinois. The primary components of
fly-ashes are given in Table 2. The typical composition range for Western bentonites that are commonly used for foundry sand binders is also included for comparison.

Reagent grade calcium hydroxide was used as an activator with the Class F fly-ash, to promote its pozzolanic reaction. The fly-ash-based binder (FBB) based on Class F fly-ash consisted of six parts by weight of fly-ash, nine parts of calcium hydroxide, and two parts of calcium nitrate. The calcium nitrate was added as an accelerator to increase the rate of the reaction. These ratios had been determined by the authors to give good binding performance in previous studies (Kawatra 2001). Calcium

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Class C fly-ash, %</th>
<th>Class F fly-ash, %</th>
<th>Western bentonite, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>34.23</td>
<td>51.67</td>
<td>58–64</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>19.53</td>
<td>26.26</td>
<td>18–21</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6.53</td>
<td>10.41</td>
<td>2.5–2.8</td>
</tr>
<tr>
<td>Total (SiO₂ + Al₂O₃ + Fe₂O₃)</td>
<td>60.29</td>
<td>88.34</td>
<td>78.5–87.8</td>
</tr>
<tr>
<td>CaO</td>
<td>25.91</td>
<td>3.12</td>
<td>0.1–1.0</td>
</tr>
<tr>
<td>MgO</td>
<td>5.00</td>
<td>0.99</td>
<td>2.5–3.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.36</td>
<td>0.62</td>
<td>1.5–2.7</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.38</td>
<td>2.59</td>
<td>2.0–2.45</td>
</tr>
<tr>
<td>Moisture, as received</td>
<td>0.06</td>
<td>0.32</td>
<td>4.5–9.0</td>
</tr>
<tr>
<td>Other</td>
<td>6.00</td>
<td>4.02</td>
<td></td>
</tr>
</tbody>
</table>
chloride would also perform well as an accelerator for the FBB, but calcium nitrate was considered to be more suitable for foundry applications, because it does not promote iron corrosion as severely as calcium chloride does.

The Class C fly-ash contained sufficient calcium in its as-received state, so that it did not require any additional activator. The fly-ash was studied both with and without calcium nitrate as an accelerator, to determine the extent to which it could increase the curing rate of the fly-ash binder.

**Equipment**

The following equipment was used for preparing and analyzing foundry sand test specimens, according to AFS specifications (AFS 1978):

- rotary sample divider, for splitting the as-received foundry sand into identical subsamples to be used in the experimental work;
- high-intensity Eirich mixer for combining foundry sand with binder, moisture, and any other desired additives: the mixer was set to operate with an impeller speed of 855 rpm;
- sand-compaction apparatus for producing an AFS standard specimen 2.000 $\pm$ 0.001 in. (50.8 $\pm$ 0.0254 mm) in diameter and 2.00 $\pm$ 1/32 in. (50.8 $\pm$ 0.794 mm) in height;
- motor-driven dead-weight-type instrument used to determine green compressive strength of the standard specimens;
- moisture teller to determine the weight percent moisture of the sand mixture.

**Procedures**

Bonded foundry-sand specimens for testing were prepared using the following procedure:

- The as-received foundry sand was divided into subsamples with identical size distributions. Each subsample weighed 8.5 lb (3.85 kg). One subsample was used for each experiment.
- Sand was weighed to the nearest 0.1 g and the necessary quantities of water, accelerator, and binder were calculated based on this weight. A constant FBB dosage of 6.5% of the dry sand weight was used in all
experiments, as this dosage is commonly used by the foundry industry (Kawatra 2001).

- For tests using an accelerator, the appropriate amount of accelerator was dissolved in the water.
- Sand and water were added to the mixer and were mixed for 30 s.
- Binder was added to the mixer and was mixed in with the sand and water for an additional 3 min.
- Test specimens were made by ramming into a steel cylinder, using the AFS standard ramming device, and were removed from the cylinder.
- Resulting test specimens were 2 in. in diameter and 2 in. tall (50.8 mm × 50.8 mm). These specimens were placed into sealed plastic containers to minimize moisture loss and were cured at 21–25°C for the desired time intervals, ranging from 1 h to 1000 h.
- Specimens were tested to determine compressive strengths and shear strengths. All specimens were prepared and measured in triplicate to ensure accuracy.

RESULTS AND DISCUSSION

A key consideration for binders to be used in foundry-mold production is the rate at which they develop the necessary strength. Studies were therefore carried out to determine how fast fly-ash binders could reach strengths that were competitive with bentonite. All binders were added at a dosage rate of 6.5% of the dry sand weight.

The results for the Class F FBB are shown in Figure 1. It was determined that, while this binder could eventually reach very high strengths, it required times in excess of 200 h before its strength would exceed the strength reached by bentonite in less than 30 min. In contrast, it can be clearly seen from the results for the Class C fly-ash, shown in Figure 2, that the Class C ash reaches a high strength after a curing time of only 2 h and when accelerator is added it can reach strengths competitive with bentonite in less than 1 h. As a result of its much higher curing rate, the Class C ash is much more practical as a replacement for bentonite binder than are binders based on Class F ash.

The faster curing time for the Class C fly-ash is due to the fact that the calcium it contains is intimately intermixed with the ash, rather than added as a separate phase as is the case for the Class F fly-ash. This intimate mixture of the components of the pozzolanic reaction results in much more rapid formation of the calcium aluminosilicate gel needed for
binding of the sand grains. It is clear from the reported results that this effect makes the Class C fly-ashes much more suitable as foundry-sand binders than the considerably slower Class F ashes. In addition, the Class F fly-ash requires calcium hydroxide to be purchased and added as a separate component. This makes its application more expensive than the use of Class C ash, which does not require the use of a separate activator.

Although the Class C ash develops its full bonding strength after much shorter curing times than the Class F ash, it is desirable to shorten the time still further. It can be seen from Figure 2 that the addition of accelerator does greatly increase the rate of strength development, as the test specimens with accelerator reached a constant level of compressive strength in less than 1 h. However, it is also evident that, while the accelerator causes strength to develop more quickly, it also reduces the peak strength that is reached. At the accelerator dosages examined (0, 6:1, and 3:1), increasing the concentration of accelerator increases the final compressive strength, but increasing to still higher dosage levels is likely to be uneconomic and so was not pursued.

It should be noted that the bentonite-bonded sand specimens reached a strength of 10.8 psi at 1 h, and that the Class C fly-ash with one part of
The Class C fly-ash reached a final strength of approximately 35 psi in 2 h with no accelerator. With a lower accelerator dosage (1/6 of the weight of the fly-ash), the final strength reached was only half as much as the strength achieved at the higher dosage (1/3 of the weight of the fly-ash), which in turn was only 20 psi, compared to the 35 psi reached in 2 h by the fly-ash with no accelerator.

CONCLUSIONS

Of the two major types of fly-ash available for use as binders (Class F and Class C), the Class F fly-ash requires greater amounts of curing time to reach full strength, although both can equal or exceed the strength achieved by bentonite binder.

Class C fly-ash develops its binding strength over a much shorter time than the Class F ash, due to differences in its basic structure and the degree of intermixing of the calcium-bearing components with the Pozzolanic aluminosilicate components. The Class C ash is, therefore, more competitive with bentonite in terms of both final strength reached and time required to reach this strength.
suitable as a foundry-sand binder, although when used alone it still requires some curing time to reach full strength.

The necessary curing time for Class C ash to reach full strength can be shortened to less than 1 h by the addition of calcium nitrate as an accelerator. While this shortens the time to reach full strength, it also reduces the maximum strength reached. However, even with the maximum strength reduced, the sand specimens made using Class C ash and accelerator still had strengths comparable to specimens made using bentonite.

REFERENCES


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