Coventry University and
The University of Wisconsin Milwaukee Centre for By-products Utilization,
Second International Conference on Sustainable Construction Materials and Technologies
June 28 - June 30, 2010, Università Politecnica delle Marche, Ancona, Italy.
Main Proceedings ed. J Zachar, P Claisse, T R Naik, E Ganjian. ISBN 978-1-4507-1490-7
http://www.claisse.info/Proceedings.htm

Improving Fly Ash Cementitious Materials for Sustainable Construction through Nanotechnology

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ABSTRACT

This paper provides an overview to several studies conducted at the Center for Advanced Cement-Based Materials that demonstrate how fly ash and nanotechnology can be incorporated in cementitious materials to yield sustainable construction materials. Fly ash has been used in cement-based materials for several decades, and has garnered attention in recent years due to environmental concerns such as reducing cement CO_2 emissions and fly ash landfill requirements. Aside from significant environmental benefits, if designed properly, concrete containing high volumes of fly ash can exhibit superior strength, durability and fresh-state properties such as flowability. However, problems such as variable material performance, unstable air-void systems and slow strength development have hindered wide use especially in the United States. The first study discussed involves the development of a nonclinker cement composed of cement kiln dust (another land-filled waste material) and class F fly ash.

INTRODUCTION

This paper summarizes studies conducted at the Center for Advanced Cement-Based Materials (ACBM) that demonstrate how fly ash can be incorporated in cementitious materials to yield sustainable construction materials. In the United States, 460 coal-fired power plants produce nearly 110 million tons of fly ash and other coal combustion products each year [ACAA 2009]. Of this total, approximately 63 million tons are land-filled. In addition to requiring large areas for disposal, land-filled fly ash can also cause environmental issues due to the possibility of leeching heavy metals which are present in fly ash into nearby water sources [NRC 2006]. Furthermore, there have been major fly ash storage collapses such as the Tennessee Valley Authority's Kingston Fossil Plant, which released over four million cubic meters of fly ash into the Emory River [Wikipedia 2009]. Cement-based materials also contribute to environmental issues. Worldwide, the cement industry is responsible for roughly 5% of the total CO_2 released yearly [Mahasenan et al. 2003]. By replacing large volumes of cement with fly ash, multiple benefits can be imparted on the environment.

Fly ash has been used in cementitious material for several decades, and has garnered attention in recent years due to environmental concerns such as reducing cement CO_2 emissions and fly ash landfill requirements. Aside from environmental benefits, if designed properly, concrete containing high volumes of fly ash can exhibit superior strength, durability and fresh-state properties such as flowability. However, problems such as variable material performance, unstable air-void systems and slow strength development have hindered wide use especially in the United States.

The first study summarized here involves the development of a nonclinker cement composed of cement kiln dust (another land-filled waste material) and class F fly ash. A mechanochemical grinding approach to increase the reactivity of fly ash was developed to increase the reactivity of the fly ash in order to achieve strength gains comparable to ordinary cements. The last two studies involve using a combination of fly ash and micro and nanoclays to improve the fresh-state properties of concrete for two specific applications: slipform paving and extrusion.

IMPROVED REACTIVITY OF CEMENT KILN DUST – FLY ASH SYSTEMS

Slow strength development has often been associated with concretes containing large volumes of fly ash. Several activation methods that aim to speed up the pozzolonic reaction include mechanical, chemical and thermal activation. Mechanical activation involves grinding fly ash, which introduces micro and nano flaws in the particles. This in turn increases the surface area of the particles, making it more reactive. Chemical activation involves adding a catalyst such as alkalis to speed up the rate of reaction. Lastly, thermal activation involves a temperature change to encourage certain reactions to occur quicker. ACBM has shown that a combination of mechanical and chemical activation techniques (mechanochemical activation) can effectively increase the reactivity of fly ash, which has allowed development of a nonclinker cement composed of cement kiln dust and fly ash [Babaian et al. 2003; Ryou et al. 2006; Bui et al. 2007; Wang et al. 2007].

Cement kiln dust (CKD) is a waste product created during the cement manufacturing process. Although nearly 75% of CKD is recycled back into the cement kiln, over 2 million tons of CKD is still land-filled each year [PCA 2009]. At ACBM, research has focused on combining CKD and class F fly ash to create a cementitious material comparable to ordinary Portland cement. The combination of CKD and fly ash is particularly synergistic since CKD contains a relatively high amount of alkalis, which provides a chemical catalyst to activate the fly ash. Class F fly ash was specifically chosen because of its higher disposal rate in comparison with class C fly ash. The combination of these waste materials was subjected to mechanochemical activation.

Experimental approach

The nonclinker mixes consisted of 65% CKD and 35% fly ash by mass, chosen for its optimal compressive strength [Babaian et al. 2003]. This composition was subjected to several different types of grinding protocols involving ball, vibratory and attrition mill grinders. The ball mill grinder consisted of a rotating porcelain jar with different alumina grinding balls [Babaian et al. 2003; Wang et al. 2007]. The rotating action applies shear forces on the particles. On the other hand, the vibratory mill consisted of a plastic bowl and alumina grinding balls [Ryou et al. 2006; Bui et al. 2007]. The vibratory nature of the system imparts direct impacts onto the particles. Lastly, the attrition mill grinder consisted of a ceramic container with a central shaft, stirring the particles as well as ceramic grinding balls [Ryou et al. 2006]. The attrition mill also applies shearing forces on the particles, but at a much higher rate than the ball mill grinder. Grinding was applied to CKD and fly ash individually as well as collectively for 0-24 hours using each type of grinder as well as combinations of each. The effects of grinding aids such as triethanolamine were also investigated [Babaian et al. 2003]. After grinding, pastes were mixed using a 0.5 water-to-binder ratio.

In order to investigate the effectiveness of both the mechanical and chemical activation methods, a collection of tests were performed to measure the particle size distribution, chemical composition, heat of hydration, set time and compressive strength at 3, 7 and 28 days.

Results

In general, all grinding methods were shown to decrease the mean particle size of the CKD-fly ash composition. In particular, improvements were documented for the percent finer than 45 microns. However, it was found that measuring the particle size distribution does not entirely indicate the effectiveness of the mechanochemical grinding. To remedy this, the chemical composition was observed using an X-ray diffraction method [Babaian et al. 2003; Ryou et al. 2006; Bui et al. 2007; Wang et al. 2007]. In this manner, the relative proportions of crystalline and amorphous phases of the composition could be determined. A higher increase in amorphous phases (or a higher decrease in crystalline phases) indicates higher reactivity. The vibratory mill grinder was much more effective in decreasing the crystalline phases when compared to the ball mill grinder [Babaian et al. 2003]. Amorphous phases remained essentially constant for all tests. Figure 1 shows the improvement of strength gain achieved by the vibratory mill over the ball mill and when no grinding was performed.

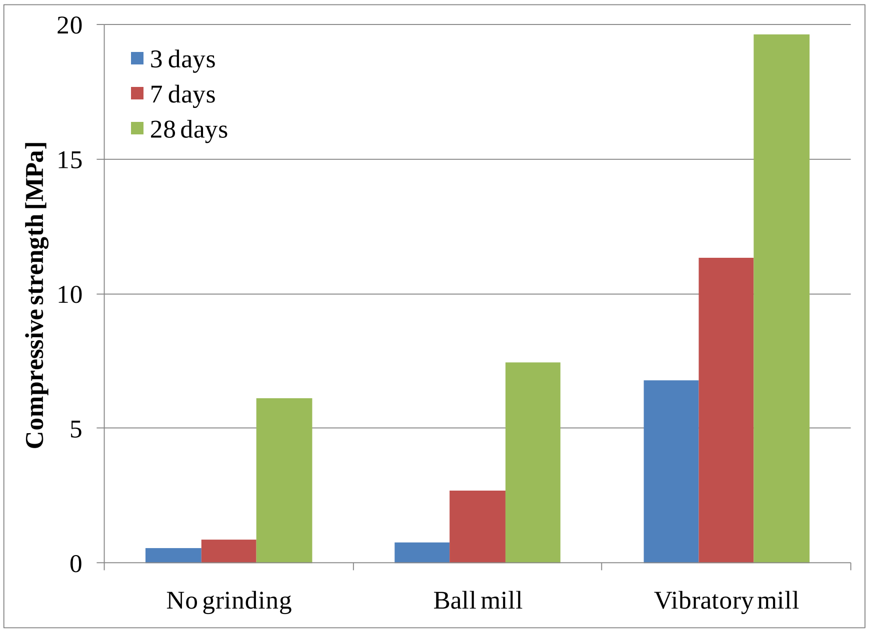

Fig. 1. Effect of different milling techniques on compressive strength gain

In comparing grinding protocols, it was found that separately grinding the CKD and fly ash produced finer particle size distributions, higher increases in amorphous phases, quicker initial set values and higher compressive strengths than grinding each component together Ryou et al. 2006; Bui et al. 2007]. Further improvements were observed for compositions that were first mixed separately, then together [Bui et al. 2007]. 28-day compressive strengths of over 20 MPa could be reached with this protocol. Figure 2 demonstrates the improvement of strength gain by combining separate and collective vibratory milling protocols.

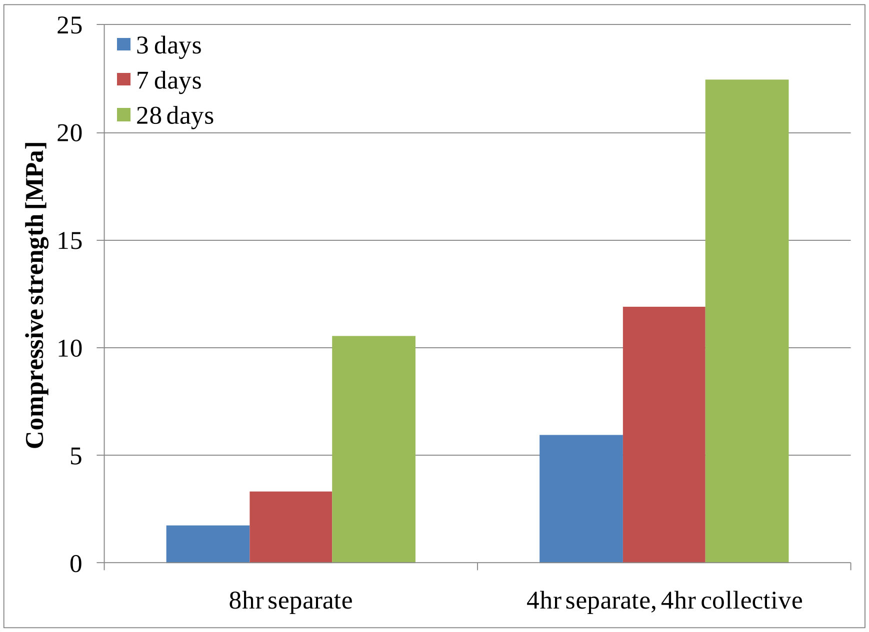

Fig. 2. Effect of milling protocols on compressive strength gain

Conclusions

Mechanochemical grinding is a technique that can overcome fly ash's slow strength gain. By combining two industrial waste products that are currently land-filled in large quantities, a nonclinker cement was produced taking advantage of the synergistic effects between the two. Optimal grinding protocols involve either separately grinding each material, or the combination of separate and collective grinding. Initial set and compressive results indicate that this cementitious material can perform comparably with typical cement-based materials.

IMPROVING FRESH-STATE PROPERTIES THROUGH USE OF FLY ASH AND CLAYS

Another focus of ACBM has been the fresh-state of concrete. Controlling properties such as flowability and shape-stability are crucial for advanced processing techniques. The next two studies summarized here involve mix compositions specifically tailored towards slipform paving and extrusion utilizing a combination of fly ash and clays to achieve desired rheological properties [Pekmezci et al. 2007; Tregger et al. 2007; Kuder and Shah 2007].

Clay properties

In addition to a class F fly ash, two clays used in current projects at ACBM are a purified magnesium alumino silicate, and a calcined, purified kaolinite, designated C1 and C2 respectively. Each commercially produced clay has a carefully controlled particle size distribution. Table 1 shows physical properties of each clay. C1 particles are needle-like with diameters of several nanometers, while C2 particles are more plate-like with thicknesses in the hundreds of nanometers.

Table 1. Clay properties

Clay	Average size, µm	Surface area, m^2/g	Specific gravity	Description
C1	1.75	150	2.62	Purified magnesium alumino silicate [AMC 2007]
C2	1.20	13	2.50	Calcined kaolinite [BASF 2009]

Improved slipform paving

Slipform paving is an efficient construction method typically used for large pavement projects such as highways. Combining placing, consolidation, forming and finishing into one process without the use of formwork, slipform paving is a process that relies on appropriate fresh-state properties of the concrete. Traditional slipform concrete requires stiff concrete with a typical slump of 50-75 mm. As a result, the concrete requires extensive internal and external vibration in order to densify the concrete.

Pavements are designed to last 25-30 years in the US, however in several areas, slipform pavements have shown significant cracks within three [Ardani et al. 2003]. These durability issues have been correlated to over-vibration from improperly operated internal vibrators. ACBM, in collaboration with the Center for Portland Cement Concrete Pavement at Iowa State University, has developed a new low-compaction energy concrete called slipform self-consolidating concrete (SFSCC), which can be slipformed without requiring consolidation from internal vibrators [Pekmezci et al. 2007; Tregger et al. 2007], thus eliminating the associated durability issues.

SFSCC requires a sufficient flowability in order to consolidate within the paver, but still must be shape-stable upon exit. Derived from basic self-consolidating concrete (SCC) design principles, supplementary materials such as fly ash and clays were added to achieve balance between flowability and shape stability while maintaining similar cement contents to those currently used in ordinary slipform mixes. SFSCC not only improves upon slipform paving in terms of durability, but also provides a valuable use for large quantities of fly ash.

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Methods and mix compositions

The two key characteristics of a SFSCC mix are flowability and shape stability, or green strength. Flowability was evaluated using the drop table test. The drop table (70×70 cm), consists of two plates hinged at one end, where the top plate can be lifted and dropped from a height of 40 mm. The test is conducted by placing a modified slump cone on the table and filling it with the fresh concrete in three layers. The cone is then removed, and after applying 15 drops, the diameter of the spread out concrete is measured. This test determines how a mix flows under external energy; for slipform applications, it is desirable for a mix to be able to flow under the least amount of energy applied before exiting the paver. In addition to determining the material flow property, the drop tables were also used to evaluate the shape stability of the mixes after compaction. This was achieved by loosely filling a 100×200 mm cylinder with concrete, placing this cylinder on the drop table and then applying 15 drops. The cylinder was demolded to evaluate its shape stability. A successful mix will not slump after compaction. Immediately after demolding, the green strength of the cylinder was determined by applying a vertical force until the specimen collapsed. The maximum force was used to calculate the green strength of the tested cylinder. A larger green strength signifies a more shape stable mix.

Table 2 shows the SFSCC mixes presented in this summary paper. Clay 1, considered a nanoclay, was used in this study along with a Type I Portland Cement, a class F fly ash, a 4.75 mm maximum size river sand, a 25 mm maximum size limestone gravel and a naphthalene-based high-range water-reducer (HRWR).

Table 2. Slipform compositions

Mix identifier	Cement, kg/m^3	Fly ash, kg/m^3	Gravel, kg/m^3	Sand, kg/m^3	Water, kg/m^3	HRWR, kg/m^3	Clay, kg/m^3
Standard slipform	353	0	897	886	151	3.5	0
SFSCC	517	0	861	794	207	2.0	0
SFSCC + FA	362	155	904	794	202	2.0	0
SFSCC + FA + C1	362	155	904	794	207	2.0	2.6

SFSCC results

The results here are summarized from [Pekmezci et al. 2007; Tregger et al. 2007]. The relationship between green strength and the flow diameter after 15 drops is presented in Figure 3. The mix labeled SFSCC contains no fly ash (FA). In order to lower the cement content, FA was added. As a result, the flowability was increased at the expense of green strength. The nanoclay, on the other hand, worked to dramatically increase the green strength while sacrificing little to the flowability; even at very small dosages.

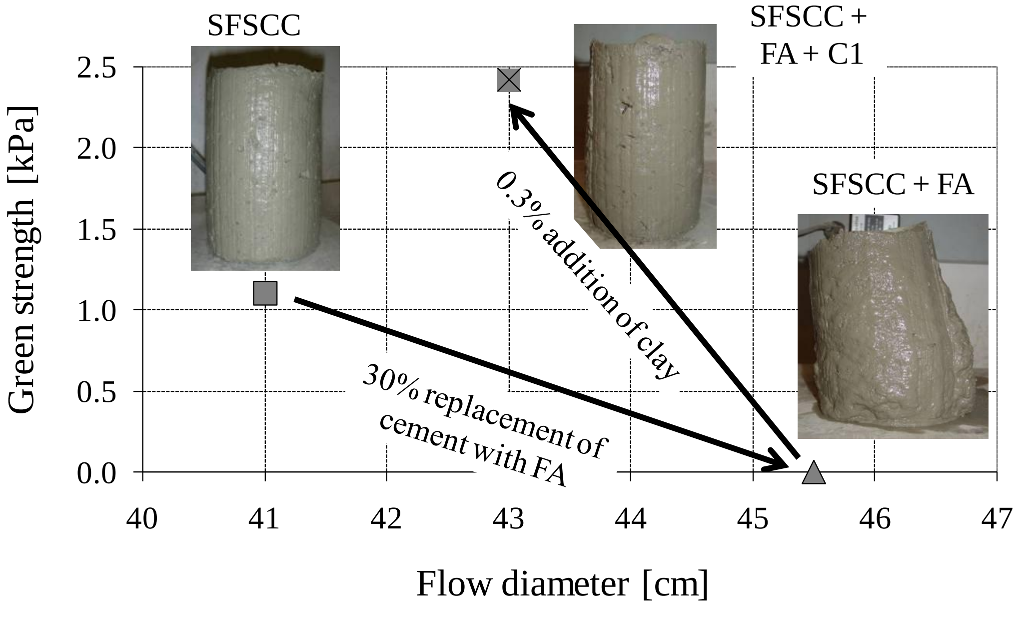

Fig. 3. Effect of clays and fly ash on green strength and flowability

In this fashion, fly ash acted not only as a cement substitute, but also to increase flowability. A combination with nanoclays achieved the appropriate rheological properties for slipform paving. Figure 4 demonstrates laboratory-scaled pavements created by a minipaver. Note that no vibration was added during pavement yet the smooth surface indicates proper consolidation while the straight edges indicate adequate green strength [Pekmezci et al. 2007].

Fig. 4. Pavement containing fly ash and clay produced without vibration.

Extruded cement-based materials

Extrusion is a processing technique that depends heavily on the rheology of the extrudate. The material must possess both adequate flowability while passing through the die and shape-stable after exiting. This technique is a convenient processing tool that consolidates the material to increase the strength to weight ratio. Mix compositions must optimize the fresh-state properties taking into consideration extruder barrel and die size as well as extrusion velocity. High-performance, fiber-reinforced cementitious composites (HPFRCC) are especially desirable due to their fire resistivity along with higher strength, durability and ductility [Peled et al. 2000; Burke and Shah 1999]. Still, because of the difficulty in achieving satisfactory rheological properties, as well as the expensive processing aids necessary (such as cellulose ethers), extrusion of cement-based materials has not been widely utilized by industry. Research at ACBM has studied the combination of fly ash and clays in maintaining satisfactory rheological properties to make extrusion of cement-based materials an attractive alternative to replace current building products [Kuder and Shah 2007]. Incorporating high volumes of fly ash have been known to increase flowability, which is required to achieve proper compaction during extrusion. In order to maintain shape-stability after extrusion, clays have been used as partial replacements for the expensive cellulose ethers.

Methods and mix compositions

Open cross-section HPFRCCs were produced using a ram-extruder with a cellular die containing two cells that had a total length of 25 mm, width of 15 mm and a wall thickness of 3.25 mm. The ram-extruder was mounted in a closed-loop hydraulic testing frame with a 24 kN load cell with a barrel diameter of 38.1 mm and a length of 125 mm. The extrusion velocity was 1 mm/s, and it should be noted that binder dosages summarized here depend on the speed of extrusion. A specimen was considered successfully extruded if the extrudate retained the die shape, resisted phase migration, avoided excessive extrusion pressure and was free of surface defects such as tearing. Mix compositions consisted of 14% Type I Portland cement, 33% fly ash, 12% silica fume, 39% water and 1% high-range water reducer (HRWR); all by volume. Two different cellulose ethers (E1, E2) and one clay (C2) were incorporated to attain sufficient shape stability at the dosages given in Table 3. E1 was a hydroxypropyl methylcellulose while E2 was a methylhydroxyethl cellulose.

Table 3. Extrusion cellulose and clay compositions by mass of binder

Mix identifier	E1 [%]	C2 [%]	Mix identifier	E2 [%]	C2 [%]
A1	0.50	0.00	B1	0.25	0.00
A2	1.00	0.00	B2	0.50	0.00
A3	2.00	0.00	B3	1.00	0.00
A4	0.50	0.15	B4	0.25	0.15
A5	0.50	0.30	B5	0.25	0.30
A6	0.50	3.00	B6	0.25	3.00

Extrusion results

The results here are summarized from [Kuder and Shah 2007]. Extrudability of the mixes are shown in Table 4. Clay C2 was effective in lowering the amount of both cellulose ethers. A clay dosage as low as 0.3% by mass of binder was required to render a mix extrudable. It was also noted that any more than 3.0% clay addition resulted in a mix prone to tearing due to excessive stiffness. Also, mixes with C2 but no cellulose ethers were not extrudable. Hence, clays can be added to replace a significant portion (here, 50%) of the cellulose ether, but cannot be used as a total replacement. However, even this amount can significantly reduce the cost of the extruded composite since the cellulose ether make up most of the cost [Kuder and Shah 2007].

Table 4. Extrudability of mixes

Mix identifier	Extrudable?	Mix identifier	Extrudable?
A1	No	B1	No
A2	Yes	B2	Yes
A3	Yes	B3	No
A4	No	B4	No
A5	Yes	B5	Yes
A6	No	B6	No

In order to gain fundamental flow properties of the extruded mixes, capillary rheology was used with the ram extruder to determine the yield stress and equilibrium viscosity. The analysis assumes that flow is laminar, fully developed and that there is no slip at the wall. The apparent shear stress ( ) and shear rate ( ) are given in Equation (1) and (2), respectively.

— (1)

—, (2)

where *P* is the extrusion pressure (kPa), *V* is the mean extrudate velocity in the capillary (mm/s), *L* is the capillary length (mm) and *D* is the capillary diameter (mm). End effects are taken into consideration using Bagley's end correction [Bagley 1957], which determines the true wall shear stress in the capillary, , by:

$$\frac{\quad}{\quad}, \tag{3}$$

where *N* is the end correction factor for the imaginary extension of the capillary length.

Capillary analysis was conducted by extruding three different die lengths at six different velocities for each mix. Three die lengths (giving L/D = 1, 2 and 4) and six piston velocities, 0.2, 0.5, 1, 2, 3 and 5 mm/s, which correspond to extrudate velocities of 1.8, 4.5, 9, 18, 27 and 45 mm/s, respectively, were used. Using capillary rheology allows flow curves to be produced, for example, Figure 5. The yield stress is calculated as the y-intercept while the equilibrium viscosity is the slope of the curve at equilibrium, i.e. when the slope no longer changes with respect to increasing the shear rate.

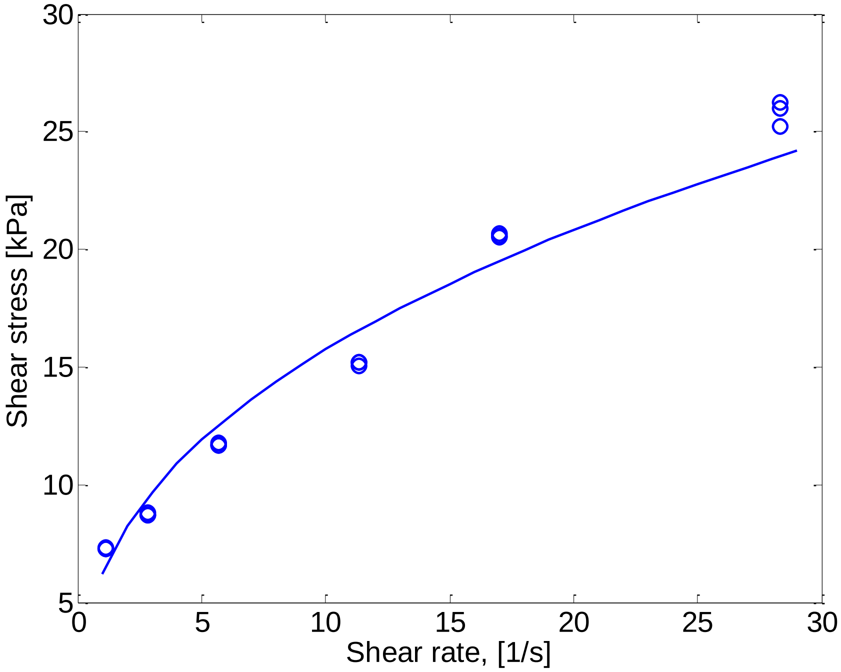

Fig. 5. Example flow curve using capillary rheology for a mix containing C2

For each mix, the yield stress could be plotted against the equilibrium viscosity, which resulted in Figure 6. The results show that acceptable extrusion is achieved for mixes with sufficient yield stress and equilibrium viscosity.

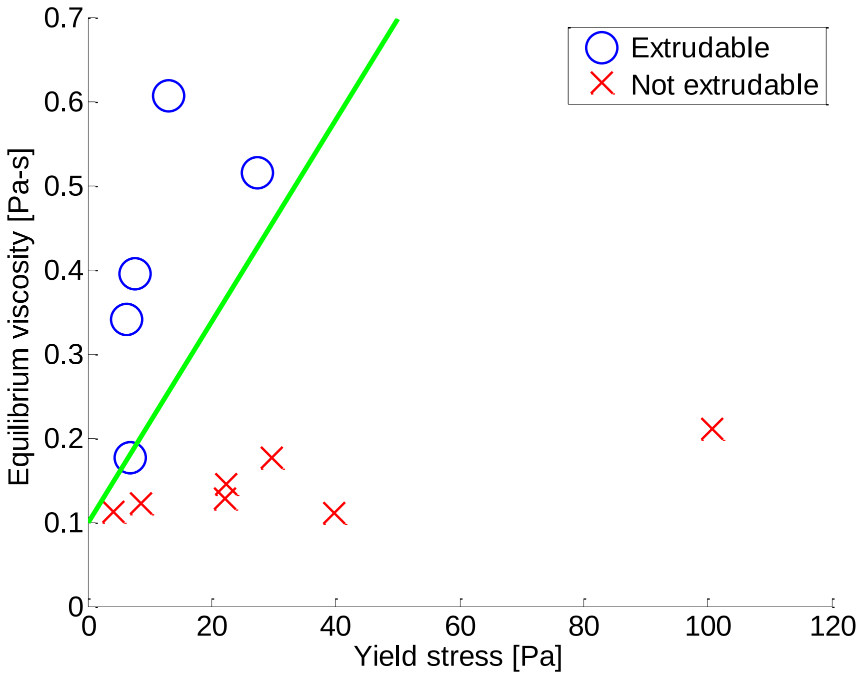

Fig. 6. Equilibrium viscosity versus yield stress for both extrudable and non-extrudable mixes

Conclusions

Both the slipform and extrusion applications demonstrated how fly ash can improve the fresh-state flowability of cementitious materials while replacing cement at large volumes. Green strength losses associated with the fly ash were recovered with the addition of very small amounts of micro and nanoclays.

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