In-Boiler Beneficiation of Coal Combustion Products for Enhanced Cementitious Value

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ABSTRACT

A novel and cost effective method for in-boiler beneficiation of coal combustion products (CCP) was developed to substantially improve cementitious value in terms of strength development of the resulting supplementary cementitious material (SCM). This process used an existing coal fired boiler with minor modifications as the source for CCP. The improved strength development characteristics enables much higher Portland cement clinker replacement levels in cement and concrete than today's typical 15-25%, thereby reducing the environmental footprint of the cementitious end product and providing an environmentally sound alternative to current wet or dry disposal methods employed for CCP. This paper presents new research and results related to strength development, durability and workability of cementitious products based on in-boiler beneficiation of CCP. The results highlight the potential benefit of using a customized, multiple input materials approach when compared to the effect of sole limestone addition as a common scrubber to control SOx emissions. In particular, the customized approach enables a selection of additions to contribute to superior strength development, durability and rheology compared to simple limestone addition. The results further indicate the possibility to produce a blended cement with the current ASTM C595 maximum 40% replacement level at similar or improved performance relative to today's typical 20% clinker replacement, or even higher replacement levels in concrete. Furthermore, since the improved strength development characteristics of the modified CCP enable higher substitution levels, many high calcium ashes that normally would not be considered ASR or sulfate friendly at 20-30% replacement may be considered ASR and sulfate durable at higher replacement levels when properly modified to offset the negative effect of elevated calcium in the parent coal.

INTRODUCTION

The concept of improving the reactivity of coal combustion products (CCP) by the addition of post-consumer and other low cost additions to a coal fired boiler at different addition points was recently described by Zacharias, Fried and Omar[1]. In summary, the method involves introducing suitable material additions into the boiler, listed in Table 1, either with the fuel feed or separately at various addition points throughout the boiler. The proper selection of type, amount, fineness and point of addition of additives controls to what extent the materials are altered in the process and hence, the reactivity of the beneficiated CCP. The environmental benefits are potentially large since the improved reactivity has the potential to allow for substantially higher clinker substitution levels with drastically lower CO_2 footprint of the resulting concrete, as well as reduced disposal of CCP in landfills or storage ponds.

Table 1. Details of materials added to the coal fired boiler[1]

Raw material addition	Average particle size, μm	Elemental composition mass % by XRF						
		SO_3	Na_2O_{eqv}	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO
Limestone	80	0	0	56	1.1	0	0	0
B	8	1.7	0.5	37	38	10	0	11
C	200	0.7	3.9	16	55	9.4	4.4	2.4
D	3	0	0.3	0	45	38	1.0	0
E	100	0.1	13.3	11	72	1.7	0	1.2
F	20	0.3	1.2	0	92	0.5	2.1	1.1

The research work presented in this paper focuses on the potential benefits of injecting materials other than limestone at various dosage and temperature levels into the coal fired boiler. Table 1 shows a non-exhaustive list of materials used in a PCC test boiler using a Powder River Basin sub-bituminous coal.

EXPERIMENTAL

Two in-boiler beneficiated CCP's were prepared using the proprietary methodology described in [1], one using primarily limestone with minor other additions and the other using a proprietary combination of the materials listed in Table 1. The details of the in-boiler beneficiated CCP's are shown in Table 2.

Table 2. Details of in-boiler beneficiated CCP's prepared

Parent coal	Sub-bituminous	
Addition type	Primarily limestone with minor other additions, kg/ton coal	Proprietary mix of materials listed in Table 1 lableled "CleanCem," kg/ton coal
	124	249
Elemental composition mass % by XRF		
SO_3	3.2	3.7
Na_2O_e	1.7	1.3
CaO	40	34
SiO_2	28	33
Al_2O_3	13	13
Fe_2O_3	3.8	5
MgO	5.6	2.9
Average particle size by laser granulometer, μm		
Average size	7.1	5.4
Estimated compounds by TGA, mass %		
$CaCO_3$	11	5.2
$Ca(OH)_2$	0.8	0.7
LOI adjusted for $CaCO_3$ and $Ca(OH)_2$ by TGA		
Adjusted LOI	0.1	0.9

Two in-boiler beneficiated CCP's and a sample of corresponding un-modified ash were tested at 30% and 60% Portland cement substitution for strength development according to ASTM C109, sulfate durability according to ASTM C1012, ASR durability according to ASTM C 1260, rheology in mortar using a mortar rheometer, and early reactivity in mortar using isothermal calorimetry. The details of the un-modified materials used are shown in Table 3. The details of the rheology and calorimetry test methods are described below:

Figure 1. Rheomixer rheology testing equipment.
Left: Rheomixer with blade mounting prior to test. Right: Ongoing rheology test with blade inserted in mortar sample.

A ConTec mortar Rheomixer was used for all rheology tests, Figure 1. Mortars were prepared using standard graded EN 196 sand and the mixing sequence in ASTM C305, with the mixture design details in Table 4.

Table 3. Details of Portland cement and un-modified fly ash

Material	Average particle size, μm	Elemental composition mass % by XRF, data from Wyoming Analytical						
		SO_3	Na_2O_e	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO
Portland Cement	24	3.1	0.5	63	21	4.4	3.6	0.7
Unmodified ASTM class C fly ash	8	4.7	2.6	30	27	18	6.3	6.7

The rheology testing was carried out in two parts:
#1 - Water demand in mortar without admixture by incremental addition of water to establish a so-called "water line", see mix design details in Table 4.
#2 - Workability retention over time for mortar mixes with a PCE based dispersant admixtures, see mix design details in Table 5.

Samples were also taken for isothermal calorimetry testing of early reactivity, hence the increased mortar volume in part #2.

Table 4. Mix designs used for water demand tests without admixture- #1

Materials	S.G.	Mass, g	Volume, ml	**Initial water/cementitious-ratio 0.5**
EN-Sand	2.62	1350	515.3	**Starting point for water demand**
Cement	3.15	299	94.9	**without admixture. Then 5%**
Fly ash	2.2	128	58.2	**incremental water additions**
Water	1	214	214	
Initial mix volume excluding air =			882	**30% fly ash in binder**
EN-Sand	2.62	1350	515.3	
Cement	3.15	163	51.7	
Fly ash	2.2	245	111.4	
Water	1	204	204	
Initial mix volume excluding air =			882	**60% fly ash in binder**

Table 5. Mix designs used for workability retention tests with admixture- #2

Materials	S.G.	Mass, g	Volume, ml	**Fixed water/cementitious-ratio 0.4**
EN-Sand	2.62	1350	515.3	**Various admixture additions**
Cement	3.15	496	157.5	**used to achieve a workable**
Fly ash	2.2	213	96.8	**mix.**
Water	1	283	283	
Mix volume excluding air =			1053	**30% fly ash in binder**
EN-Sand	2.62	1350	515.3	
Cement	3.15	280	88.9	
Fly ash	2.2	420	190.9	
Water	1	280	280	
Mix volume excluding air =			1075	**60% fly ash in binder**

RESULTS

The strength development in ASTM C109 mortar with 0%, 30% and 60% substitution of Portland cement is shown in Figure 2.
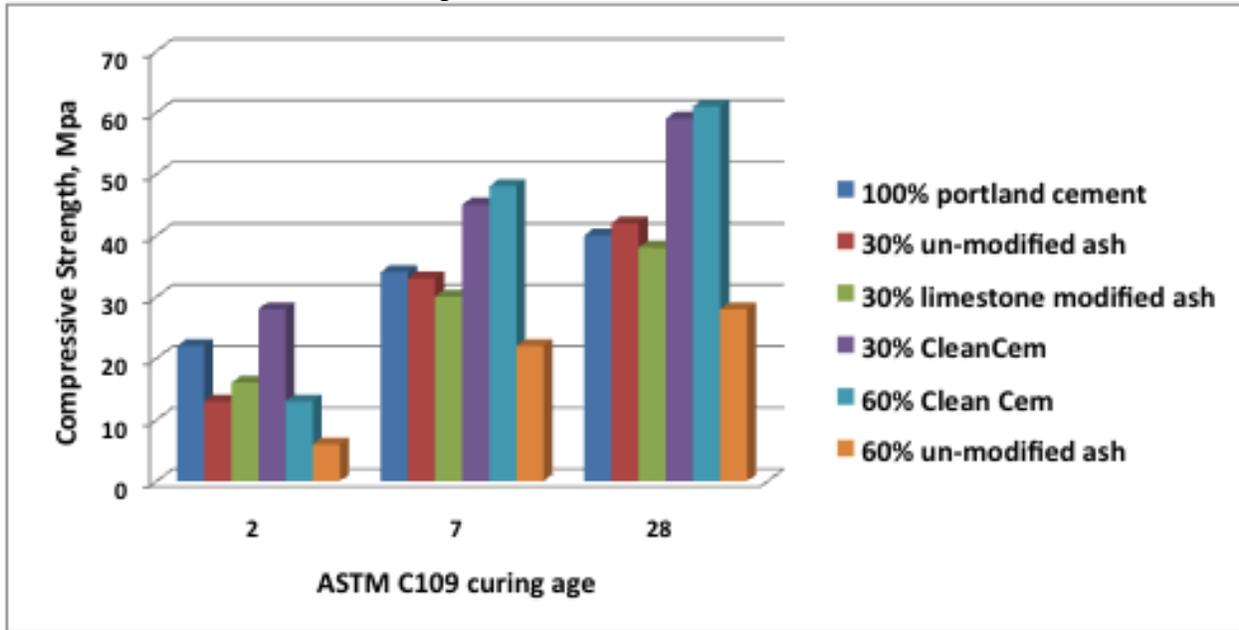

Figure 2. Compressive strength development in ASTM C109 mortar.

The results from ASTM C1012 sulfate exposure tests of mortar with 30% or 60% substitution of Portland cement are shown in Figure 3.
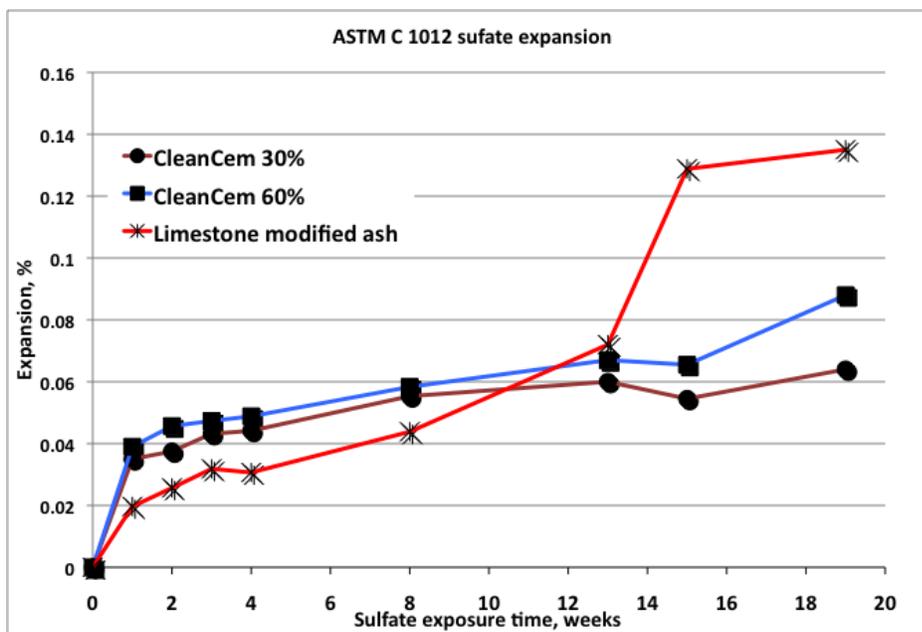

Figure 3. Mortar bar expansion in ASTM C1012 sulfate exposure tests

The results from ASTM C1260 ASR expansion tests of mortar with 0%, 30% and 60% substitution of Portland cement are shown in Figure 4.
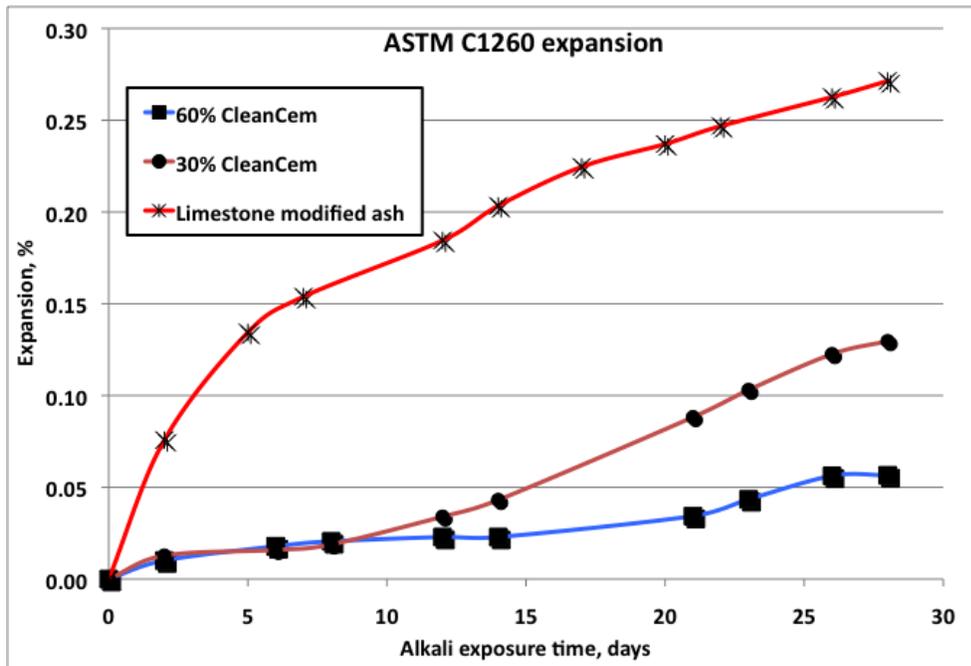
Figure 4. Mortar bar expansion in ASTM C1260 tests for expansion due to alkali-silica reaction

The results from rheology testing of water demand of mortar with 30% and 60% substitution of Portland cement tested without admixture are shown in Figure 5.
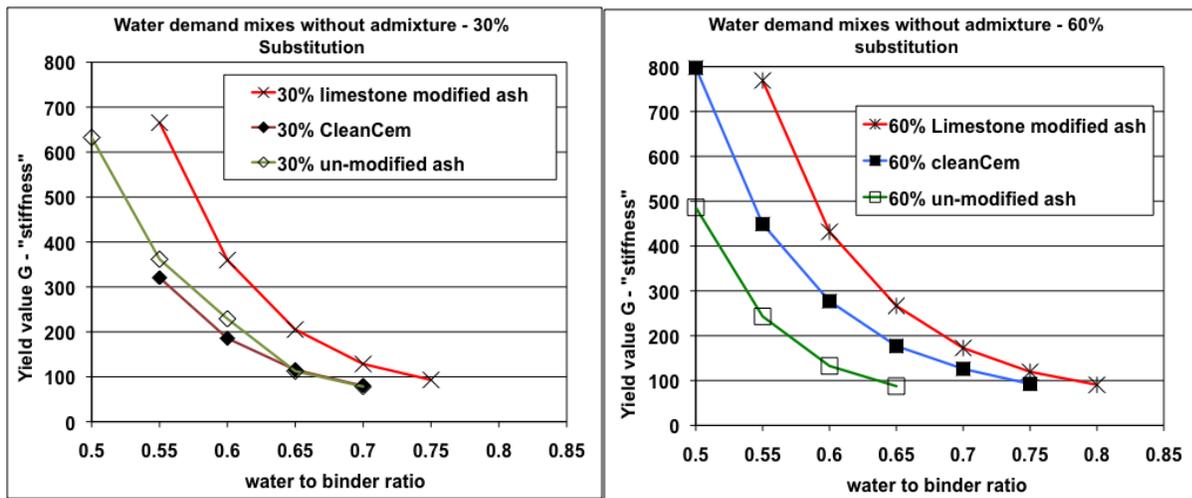
Figure 5. Water demand for mixes without admixture.

The results from rheology testing of the loss of workability (stiffening) with time for mortar with 30% and 60% substitution of Portland cement tested with PCE based dispersing admixture dosed to give a workable mix at the beginning of each test are shown in Figure 6.

Figure 6. Stiffening over time of mortar mixes with PCE based dispersing admixture dosed to give a workable mix at the beginning of each test.

Figure 7 shows the early reactivity of mortar mixes with PCE based dispersing admixture measured by isothermal calorimetry at 20º C.
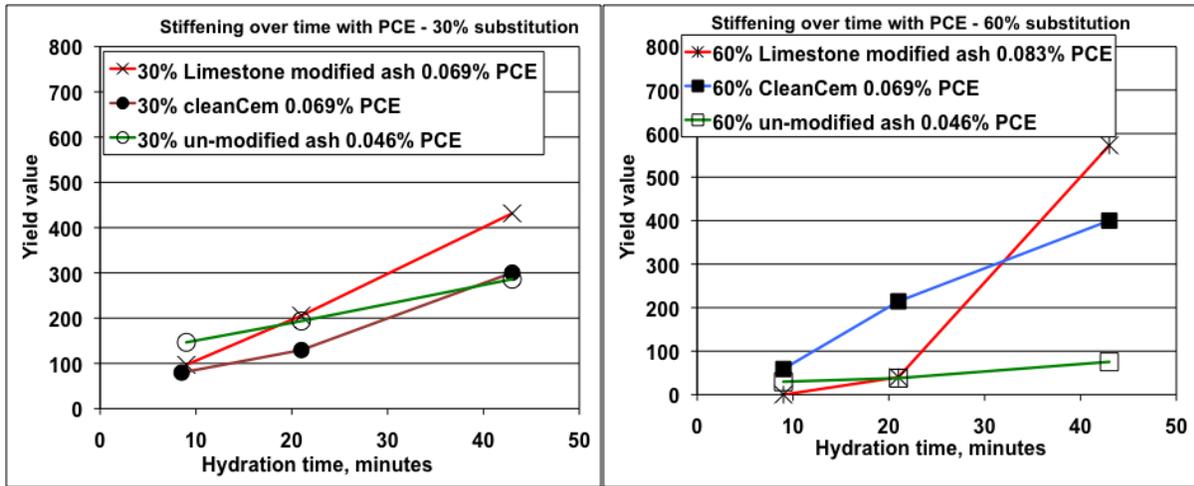

#1 mortar 30% Limestone modified ash 0.069% s/s PCE w/c 0.40 at 20 C
#2 mortar 60% Limestone modified ash 0.083% s/s/ PCE w/c 0.40 at 20 C
#3 mortar 30% CleanCem 0.069% PCE w/c 0.40 at 20 C
#4 mortar 60% CleanCem 0.069% PCE w/c 0.40 at 20 C
#5 mortar 30% un-modified ash 0.046% PCE w/c 0.40 at 20 C
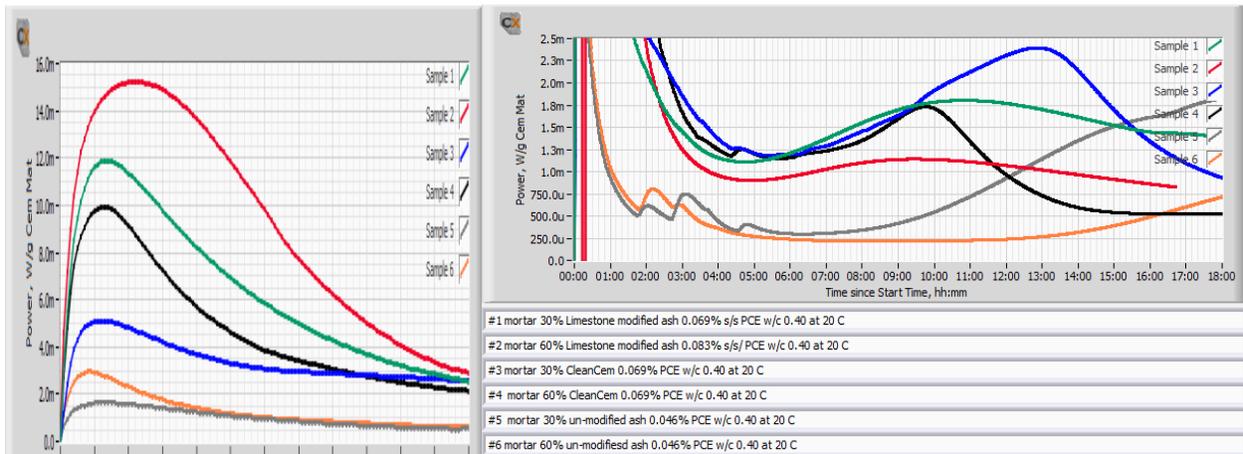#6 mortar 60% un-modifiesd ash 0.046% PCE w/c 0.40 at 20 C

Figure 7. Early reactivity of mortar mixes with PCE based admixture measured by isothermal calorimetry at 20º C. Left: Reactivity at 0-2 hours affecting workability loss. Right: Reactivity after 2 hours affecting set and compressive strength development.

DISCUSSION

In ASTM C109 compressive strength tests, CleanCem in-boiler modified ash tested at 30% substitution and 60% substitution outperformed both the unmodified and the limestone treated ash at all ages and pure Portland cement at 7 and 28 days. The higher levels of reactivity are likely due to a combination of the altered chemical composition, the creation of additional amorphous phases and smaller particle sizes

from comminution induced by the material addition at specific injection points in the boiler.

CleanCem treated ash also markedly outperformed limestone treated ash in durability testing, both in sulfate resistance and ASR mitigation testing, due in part to the presence of aluminosilicates formed by dehydroxylation of the kaolin in the process.

The calorimetry results reveal the increased early reactivity of in-boiler modified ash in terms of increased heat generation at early age compared to the un-modified ash. Note that the typical retardation of the Portland cement hydration peak caused by un-modified class C ash is not seen for in-boiler modified ash, possibly due to the effect of nucleation caused by reactive particles and increased surface area.

Despite the enhanced reactivity, the water demand for mixes with CleanCem in-boiler modified ash were similar or only slightly higher compared to un-modified ash. However, the water demand mixes with limestone modified ash were significantly higher compared to un-modified ash. Most likely, the higher water demand for the limestone modified ash is linked to a higher free lime and calcium sulfate anhydrite content as a result of the limestone addition. When tested for loss of workability (stiffening) over time with PCE based admixture, no significant loss of workability was seen at 30% replacement. However, at 60% replacement the loss of workability was significant, especially for the mix with limestone modified ash.

CONCLUSION

The tests conducted and the data generated show that a coal fired boiler can be used as a co-generator to produce a highly reactive pozzolanic material obtained by thermal blending and comminution of existing ash particles and select additives introduced into the boiler. The dosage rates, particle sizes and injection points in a PCC boiler burning a sub-bituminous coal can be selected so as to produce a material of superior quality to the untreated ash obtained in a traditional combustion / scrubber configuration.

While the compressive strength and durability performance of untreated and/or limestone (scrubber) treated ash are inadequate for use at 60%, or even 30% cement substitution, the modified CleanCem material reached performance levels that meet or exceed the criteria to enable its use at high substitution rates, with the ensuing mitigating effect on ash disposal rates and CO_2 emissions.

REFERENCES

[1] M. Zacharias, W. Fried, K. Omar, Method for converting coal ash into a high performance cement substitute utilizing sorbent injection, Proceedings of the American Flame Research Committee Pacific Rim Combustion Symposium, Maui, HI, September 26-29, 2010.