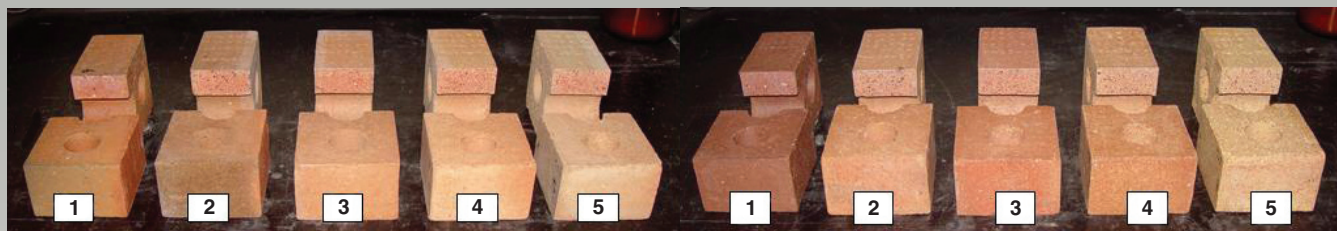


Manufacturing Bricks with Fly Ash and Advanced Coal Combustion By-products

Mei-In Melissa Chou, Sheng-Fu Joseph Chou, Lu-Ming Chen, and Joseph W. Stucki



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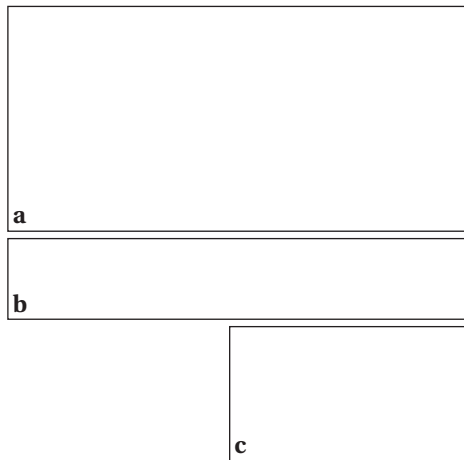


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Front Cover: (a) and (b) Full-size bricks, sawn in half, after firing. (c) Full-size bricks before firing.

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Abstract

This study investigated the use of bottom ash or flue gas desulfurization (FGD) sulfite and sulfate coal combustion by-products (FGD-sulfite and FGD-sulfate CCBs) instead of, or in combination with, fly ash in the production of high-quality building bricks. Various combinations of fly ash, bottom ash, FGD-sulfite, and FGD-sulfate were used as partial substitutes for the shale component of bricks. Commercial-size fired bricks made with these substituted materials had good physical appearance without scum, lime pops, cracks, black hearts, or red hearts. The majority of the test bricks met the ASTM classification for severe-weathering grade; the remainder were acceptable for moderate- or negligible-weathering grade. Bricks containing FGD-sulfite were whiter and had lower compressive strength and greater water absorption capacity than regular fired bricks without CCBs. The fired bricks containing blends of fly ash and bottom ash were comparable in color to regular fired bricks without CCBs. In particular, the addition of bottom ash to the brick composition increased brick redness, improved compressive strength, and decreased water absorption capacity.

All of the fired bricks containing CCBs produced in these tests can be considered to be environmentally safe construction products. The fly ash and bottom ash from our specific project source can be recommended for use in making fired bricks. To fully evaluate the environmental impact of using higher-sulfur content FGD CCBs as an ingredient in fired bricks, further studies are warranted to determine the fate of the sulfur during brick firing.

Introduction

More than 122 million tons of coal combustion by-products (CCBs) are produced nationwide each year by coal-burning utilities that generate electricity. About 60% of these CCBs are disposed of as waste (American Coal Ash Association 2006). In addition to fly ash and bottom ash CCBs, the annual production of flue gas desulfurization (FGD) CCBs is expected to continue to increase as more utilities add

FGD systems to their existing plants or build new plants with FGD systems in order to meet more stringent nitrogen oxide and sulfur dioxide standards. A portion of the high-quality FGD sulfate CCBs (FGD-sulfate) is similar to mined gypsum and is used by the wallboard industry (American Coal Ash Association 2006). However, additional amounts of high-quality FGD CCBs and most of the low-quality FGD CCBs (FGD-sulfite) are discarded in landfills. As more utility plants adopt FGD technologies, the production of both high-quality and low-quality FGD solid CCBs will increase sharply, requiring more landfill space and increasing disposal costs. Consequently, value-added applications are needed to expand the utilization of these CCBs.

A previous study developed high-quality, marketable fired bricks containing high volumes of Class F fly ash generated from burning Illinois Basin coals (Chou et al. 2005, 2006a, 2006b). The brick-making process used fly ash as a raw material substituting for part of the shale component. Clay and shale are the two primary ingredients used to make conventional fired bricks. Bricks containing fly ash at up to 40 vol% have been successfully produced in commercial-scale production test runs. The fired bricks met or exceeded ASTM standard specifications (ASTM 2005). This present study investigated the possible use of CCBs other than fly ash, or in combination with fly ash, for the production of high-quality building bricks.

Experimental Procedures

Sample Acquisition

Seven CCB samples were acquired from four different sources that burn Illinois Basin coals—two in Illinois (Utilities A and C) and two in Indiana (Utilities B and D). The sample number, source, and a brief description of these CCB samples are listed in Table 1.

The FGD-sulfite material from Utility A had been

discharged together with the fly ash into a storage pond prior to permanent disposal at off-site locations. Therefore, the ponded sample (RAW-1) received from Utility A was a mixture of the FGD-sulfite material and fly ash. The FGD-sulfite collected from Utility B had been stabilized (conditioned) by the addition of about 30% fly ash and 3% lime prior to its disposal. Samples of FGD-sulfite were acquired from Utility B before (RAW-3) and after (RAW-2) conditioning. The FGD-sulfate (FGD-formed gypsum) from Utility C was collected and identified as RAW-4. The dry fly ash sample from Utility C, collected from an electrostatic precipitator, was identified as RAW-5. The fly ash and bottom ash of Utility D had been discharged into a common holding pond. Because bottom ash contains large, dense particles that settle near the discharge point and finer fly ash particles settle farther away from the discharge point, the bottom ash sample (RAW-7) was collected near the discharge point, and the fly ash sample (RAW-6) was collected from the opposite end of the pond, farthest from the discharge point.

The CCB samples were acquired in buckets (40 pounds per bucket) and processed for analyses. An FGD-sulfate (FGD-formed gypsum) sample from the University of Illinois' Abbott Power Plant in Champaign was used as the reference standard sample in the X-ray diffraction (XRD) analysis of the FGD-sulfate material (FGD-formed gypsum) from Utility C. The purity of the Abbott Power Plant sample was >98% (Chou et al. 1998). All raw materials except RAW-3 and RAW-5 were evaluated for their use in brick making.

Table 1 Sample identification, utility source, and description of the raw materials and coal combustion by-product samples.

Sample	Utility	Description ¹
RAW-1	A	FGD-sulfite ponded with fly ash
RAW-2	B	FGD-sulfite, conditioned
RAW-3	B	FGD-sulfite, unconditioned
RAW-4	C	FGD-sulfate material (gypsum)
RAW-5	C	Dry fly ash
RAW-6	D	Ponded fly ash
RAW-7	D	Ponded bottom ash

¹FGD, flue gas desulfurization.

Characterization of Materials and Products

The chemical analyses of raw materials included analyses of major, minor, and trace elements (including sulfur and mercury); carbon was measured as loss on ignition (LOI). In addition, samples of full-size test bricks before and after firing were pulverized and analyzed for chemical composition. Samples of the final fired bricks with optimized formulations for potential commercial production were pulverized and subjected to a simulated acid rainwater extraction, followed by element analysis of the extracts, to determine the environmental impact of the production process.

Chemical analyses were conducted at the Illinois State Geological Survey (ISGS) analytical laboratory, a University of Illinois at Urbana-Champaign laboratory, the Illinois Waste Management Research Center (now the Illinois Sustainable Technology Center) laboratory, and the ALS Chemex commercial laboratory. At least one of these laboratories was equipped with the following instruments: an inductively coupled plasma spectrometer, an atomic emission spectrometer for analyzing 30 elements, an X-ray fluorescence spectrometer for analysis of major elements as metal oxides, an X-ray diffractometer for mineralogical characterization of the samples, a scanning electronic microscope for particle image analysis, and a cold-vapor atomic absorption spectrometer for mercury analysis.

Fired bricks from the bench-scale and commercial firing runs were first analyzed for color, shrinkage, physical appearance, and marketability based on the participating brick plant's specifications. Following visual inspections, engineering properties of these bricks were tested. Water absorption and compressive strength were tested according to the ASTM C67 standard method (ASTM 2007). Data were evaluated according to ASTM C62 specifications (Table 2) (ASTM 2005). ASTM standard methods were used to ensure appropriate comparisons between bricks made with and without CCBs.

Table 2 ASTM C62 standard specifications for building bricks (ASTM 2005).

ASTM C62 Classification ³	Minimum compressive strength (psi)		Maximum 24-h cold water absorption (≤ 8 wt%) ¹			
			Maximum 5-h boiling water absorption (wt%)		Maximum saturation coefficient ²	
	5-brick average	Individual brick	5-brick average	Individual brick	5-brick average	Individual brick
SW	3,000	2,500	17	20	0.78	0.80
MW	2,500	2,200	22	25	0.88	0.90
NW	1,500	1,250	no limit	no limit	no limit	no limit

¹If the cold water absorption does not exceed 8 wt%, then the boiling water absorption and saturation coefficient specifications are waived.

²The saturation coefficient is the ratio of absorption by 24-hour submersion in cold water to the absorption after 5-hour submersion in boiling water.

³Classification: SW, severe weathering; MW, moderate weathering; NW, negligible weathering.

Production of Full-Size Green Bricks and Fired Bricks

Batch 1 Runs

Small batches of full-size ($4 \times 2.5 \times 8.25$ inches) green building bricks were produced by a proprietary mold-press method. For each formulation, three identical green bricks were made. One was fired at the ISGS, and the other two bricks were fired as part of commercial firings at Brick Plant I (BP-I) and Brick Plant II (BP-II).

The feed formulations for the Batch 1 runs are indicated in Table 3. A reference standard formulation containing only clay and shale and no CCB (brick formulation 1) was included in the test runs for comparison. All other bricks contained 10 wt% of clay and various amounts of CCBs substituted for part of the shale (Table 3). Brick formulation 2 contained 25 wt% of RAW-1 (FGD-sulfite material of Utility A) and 15 wt% of RAW-7 (bottom ash) balanced with the shale. Brick formulations 3, 4, and 5 contained RAW-1 at 20, 30, and 40 wt%, respectively, balanced with the shale.

Batch 2 Runs

In the Batch 2 runs, brick formulations containing fly ash (RAW-6), bottom ash (RAW-7), conditioned FGD-sulfite (RAW-2), and FGD-sulfate (gypsum) (RAW-4) were tested for fired brick making (Table 4). One reference standard brick formulation was included for comparison. Mold-pressed full-size green building bricks were made at the ISGS and fired as part of a commercial firing run by BP-I. BP-I formulated its fired bricks based on volume ratios. The weight percent equivalents were calculated, and both measures are indicated in Table 4. The reference standard brick formulation (Brick 7) contained a 1:6 mixture of BP-I clay and BP-I shale (14.29:85.71 vol%).

As mentioned earlier, the fly ash and the bottom ash from Utility D were discharged into a common holding

Table 3 Feed formulations (wt%) for Batch 1 runs at Brick Plants I and II.

Brick formulation	Clay	Shale	Bottom ash (RAW-7)	FGD-sulfite ¹ (RAW-1)
1 ²	10	90	0	0
2	10	50	15	25
3	10	70	0	20
4	10	60	0	30
5	10	50	0	40

¹Flue gas desulfurization (FGD) sulfite coal combustion by-product.

²Reference standard.

pond, and the fly ash and bottom ash were sampled separately from different locations in the pond. To understand how the amount of bottom ash affected the quality of the fired bricks, we evaluated formulations with various mixes of fly ash and bottom ash (brick formulations 1 through 4).

The engineering properties of the fired bricks were determined using ASTM (2007) standard test methods for absorption and compressive strength and were evaluated according to ASTM C62 classification (ASTM 2005).

Environmental Assessment

The possible environmental impacts of using fired bricks containing CCBs generated from burning Illinois Basin coal were assessed by means of extraction experiments conducted on pulverized fired brick samples (-60 mesh) according to U.S. EPA Method 1320 (U.S. Environmental Protection Agency 1986). Pulverized samples of three selected fired bricks (Bricks 4, 6, and 10) from Batch 2 runs were agitated in simulated acid rainwater for 24 hours. The concentrations of 20 elements were determined, including arsenic, boron, cadmium, chromium, mercury, nickel, and lead, in the extracts from these samples. The element composition of the extracts generated from simulated acid rainwater extraction was analyzed using the inductively coupled plasma spectrometer, an atomic emission spectrometer, and/or an atomic absorption spectrometer. A cold-vapor atomic absorption spectrometer was used for mercury determination.

Economic Assessment

An economic assessment was conducted for production of bricks containing CCBs, particularly fly ash and bottom ash. Factors considered included current plant costs and the transportation costs associated with shipping ash. Because both fly ash and bottom ash are ponded or landfilled as waste, the major cost to the brick

Table 4 Feed formulations for Batch 2 runs at Brick Plant I (BP-I).

Brick formulation	Unit	BP-I clay	BP-I shale	Fly ash (RAW-6)	Bottom ash (RAW-7)	FGD-sulfite ¹ (RAW-2)	FGD-sulfate ¹ (RAW-4)
1	vol%	14.29	42.86	14.29	28.57	-	-
	wt%	16.70	46.31	12.50	24.49	-	-
2	vol%	14.29	42.86	28.57	14.29	-	-
	wt%	16.47	47.02	28.57	12.62	-	-
3	vol%	14.29	57.13	14.29	14.29	-	-
	wt%	15.59	58.85	12.55	13.01	-	-
4	vol%	14.29	28.57	28.57	28.57	-	-
	wt%	16.32	31.71	25.59	26.38	-	-
5	vol%	14.29	57.14	-	14.29	14.29	-
	wt%	16.89	63.87	-	13.21	6.03	-
6	vol%	14.29	42.85	28.58	-	14.29	-
	wt%	16.29	50.93	26.74	-	6.04	-
7 ²	vol%	14.29	85.71	-	-	-	-
	wt%	14.96	85.04	-	-	-	-
8	vol%	14.29	71.42	-	-	14.29	-
	wt%	16.55	77.56	-	-	5.89	-
9	vol%	14.29	57.14	-	-	28.57	-
	wt%	18.24	68.93	-	-	12.83	-
10	vol%	14.29	71.42	-	-	-	14.29
	wt%	16.01	70.09	-	-	-	13.90

¹Flue gas desulfurization (FGD) sulfite and sulfate coal combustion by-product samples.

²Reference standard brick formulation without coal combustion by-products.

company for obtaining the ash is transportation. The possibility of obtaining shipping and production cost incentives also must be evaluated on a case-by-case basis. However, no new major equipment is needed to retrofit existing brick plant machinery to use CCBs. Each brick company that partnered in this study has an existing source of CCBs and could readily market CCB-containing brick products to meet or exceed conventional brick specifications.

Results and Discussion

Raw Materials and Characterization

Chemical Analyses

The samples were analyzed for their major, minor, and trace element composition. Table 5 lists the major metal oxide composition and carbon content, measured as LOI for the CCB samples and BP-I clay and shale samples. Table 5 also shows the sulfur and mercury contents of the CCB samples. The con-

centrations of 15 other elements in the samples are shown in Table 6. The dry fly ash sample, RAW-5, was not analyzed, other than XRD, because it was not tested as a brick ingredient in this project.

As indicated in Table 5, the samples containing FGD-sulfite or FGD-sulfate (RAW-1, RAW-2, RAW-3, and RAW-4) had calcium oxide (CaO) values ranging from 26.29% to 38.87%. The ponded fly ash sample (RAW-6) and bottom ash sample (RAW-7) had CaO values of 1.19% and 7.22%, respectively. The CaO values of the clay and shale samples were <0.8%. The samples containing FGD-sulfite or FGD-sulfate materials (RAW-1, RAW-2, RAW-3, and RAW-4) had lower silicon oxide (SiO₂), aluminum oxide (Al₂O₃), and iron oxide (Fe₂O₃) values than the remaining samples. The SiO₂ contents were ≤21%, the Al₂O₃ contents were ≤6.15%, and the Fe₂O₃ values were ≤6%. Evidently, conditioning (RAW-2) added quantities of SiO₂, Al₂O₃, and Fe₂O₃ to the FGD-sulfite sample (RAW-3), which is reflected by the metal oxide values

Table 5 Metal oxide composition, loss on ignition (LOI) value, and sulfur and mercury contents of the coal combustion by-product samples (given as wt% except as indicated).^{1,2}

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	S ¹	Hg (mg/kg)
RAW-1	17.21	6.15	5.68	0.30	0.02	0.58	26.29	0.57	0.71	0.09	15.00	14.20	0.18
RAW-2	13.93	6.15	6.00	0.27	0.01	1.30	30.03	0.71	0.77	0.07	8.17	14.10	0.36
RAW-3	2.89	0.54	0.45	<0.01	0.01	1.99	38.87	0.10	0.02	0.04	4.25	20.80	0.44
RAW-4	0.85	0.16	0.15	<0.01	<0.01	0.15	34.79	0.06	0.02	0.06	17.35	21.30	0.21
RAW-6	53.57	23.86	12.88	1.24	0.03	1.15	1.19	0.71	2.70	0.16	1.86	0.04	0.02
RAW-7	46.49	21.23	17.25	1.12	0.11	0.95	7.22	1.03	1.75	0.06	1.10	0.57	0.05
BP-I clay	58.21	20.85	5.48	1.17	0.08	1.31	0.70	0.46	2.36	0.12	9.06	0.28	0.06
BP-I shale	59.87	17.98	6.74	1.07	0.10	1.82	0.71	0.94	2.97	0.17	7.28	0.23	0.02
BP-I clay and shale	59.64	18.29	6.49	1.10	0.12	1.91	0.61	0.85	3.08	0.16	7.46	0.22	0.03

¹The sulfur dioxide value is 2 × S (sulfur content), wt%.

²SiO₂, silicon oxide; Al₂O₃, aluminum oxide; Fe₂O₃, iron oxide; TiO₂, titanium dioxide; MnO, manganese oxide; MgO, magnesium oxide; CaO, calcium oxide; Na₂O, sodium oxide; K₂O, potassium oxide; P₂O₅, phosphorus pentoxide; LOI, loss on ignition; S, sulfur; Hg, mercury.

Table 6 Concentrations of elements in the coal combustion by-product samples (mg/kg except as indicated).¹

Sample	As	B	Ba	Ca (wt%)	Cd	Cr	Li	Ni	Pb	K (wt%)	Na (wt%)	Mg (wt%)	Mn	Sr	Zn
RAW-1	9.0	1,360	110	17.60	1.48	74	15.8	39	15.8	0.65	0.41	0.33	171	179	139
RAW-2	46.0	510	60	20.30	0.93	64	36.2	71	55.1	0.69	0.57	0.82	151	324	118
RAW-3	<5.0	280	30	26.10	0.44	9	4.5	<1	4.7	0.10	0.03	1.31	143	332	35
RAW-4	<5.0	20	<10	15.50	0.02	37	0.6	<1	1.9	0.03	<0.01	0.07	17	78	4
RAW-6	89.7	450	550	0.82	3.74	239	154.5	260	168.5	2.11	0.48	0.59	244	345	517
RAW-7	21.9	ND ²	480	5.17	0.50	211	169.5	233	69.5	1.47	0.83	0.50	886	353	341
BP-I clay	15.1	114	440	0.45	0.05	94	214.0	65	28.2	1.78	0.34	0.74	629	282	64
BP-I shale	10.2	ND	480	0.48	0.22	68	88.0	54	23.2	2.22	0.67	1.01	683	150	105
BP-I clay and shale	4.4	ND	440	0.33	0.11	61	87.8	50	21.9	2.35	0.63	0.98	578	159	91

¹As, arsenic; B, boron; Ba, barium; Ca, calcium; Cd, cadmium; Cr, chromium; Li, lithium; Ni, nickel; Pb, lead; K, potassium; Na, sodium; Mg, magnesium; Mn, manganese; Sr, strontium; Zn, zinc.

²ND, Not determined.

for sample RAW-2. The ponded fly ash sample (RAW-6) and the ponded bottom ash sample (RAW-7), like the clay and shale samples, had SiO₂, Al₂O₃, and Fe₂O₃ as their major metal oxides.

For the samples containing FGD by-products (RAW-1, RAW-2, RAW-3, and RAW-4), calcium contents ranged from 15.50 to 26.10% (Table 6), and sulfur contents ranged from 14.10 to 21.30% (Table 5), reflecting the calcium sulfate or calcium sulfite present in the FGD materials. Mercury contents of these four samples ranged from 0.18 to 0.44 mg/kg (Table 5). The fly ash and bottom ash samples (RAW-6 and RAW-7) and the clay and shale samples

all had calcium contents of ≤5.17%, sulfur contents of ≤0.57%, and mercury contents of ≤0.06 mg/kg. For the 15 other elements determined, no specific similarities or differences could be found between the CCB samples and the clay or shale samples.

X-ray Diffraction Analysis

The major mineralogical composition of the raw materials was determined by XRD analyses. The fly ash, clay, and shale samples were analyzed at the ISGS XRD laboratory. Typical X-ray diffractograms from a dry fly ash (powder fly ash) sample and a ponded fly ash

sample are shown in Figure 1; they appear to be similar. The diffractograms for the shale, clay, and mixed shale and clay samples are shown in Figure 2.

Because fly ash samples were subjected during coal combustion to heat high enough to cause some melting of the minerals present, the diffractograms of the fly ashes (Figure 1) show a mixture of crystalline and amorphous materials. The crystalline components include quartz that escaped melting and minerals such as mullite, hematite, and magnetite that formed at high temperature during coal combustion.

The diffractograms of the shale sample, the clay sample, and the mixed shale and clay sample (Figure 2) show peaks for chlorite, illite, kaolinite, quartz, K-feldspar, plagioclase feldspar, and all other clay minerals. The shale and clay samples contained refractory minerals that do not melt at brick-firing temperatures and generally larger particles (kaolinite and quartz) that help to maintain the brick's body shape during firing. The shale and clay samples also contained enough minerals with lower melting points (i.e., feldspars, chlorite, and iron-rich illite) to melt and form a steel-hard body with low water absorption.

Based on these XRD analyses, the resulting semi-quantitative mineral composition data, including the clay index (CI) of the clay, the shale-clay mix, and the ponded fly ash samples, are listed in Table 7. The CI is the sum of clay mineral percents [illite + kaolinite + chlorite] divided by 100. The CI provides a relative measure of the extrudability of feed materials; a higher value represents greater extrudability. The feed materials should have adequate extrudability (a CI value of about 0.4 would meet BP-I's requirement) in order to form strong and firm green bricks for firing. Based on a survey of more than half of the participating brick manufacturing plants in the United States, the primary method of forming green bricks is extrusion (93.2%) (Brick Industry Association 2006).

The mineral composition data (Table 7) indicate that the BP-I clay had the greatest CI (0.61), and the BP-I clay-shale mixture had a CI of 0.41. Fly ash, which functions as filler for the brick body, does not improve extrudability.

Samples of bottom ash, FGD-sulfite, and FGD-sulfate (gypsum) were analyzed by XRD at the XRD facility at the University of Illinois. The X-ray diffractograms of samples collected from different time periods were compared to examine sampling consistency in mineral composition over time. The X-ray diffractograms of both the conditioned FGD-sulfite samples (RAW-2) and the unconditioned FGD-sulfite

materials (RAW-3) collected from the same sources a year apart showed very similar peak distribution patterns. This result suggested that there was no notable mineralogical change in the

FGD-sulfite material over the sampling time and that the utility plant could supply consistent raw feed materials over time.

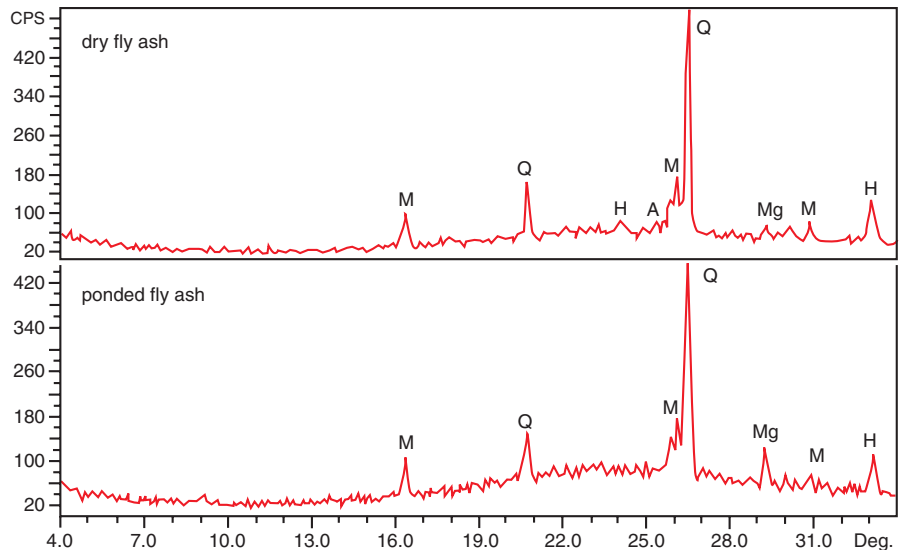


Figure 1 X-ray diffractograms of dry fly ash and ponded fly ash samples. The mineral peak indications are mullite (M), quartz (Q), hematite (H), anatase (A), and magnetite (Mg). The broad “hump” in the background between about 13 and 30 degrees 2θ is due to abundant noncrystalline glass in the samples. CPS, counts per second.

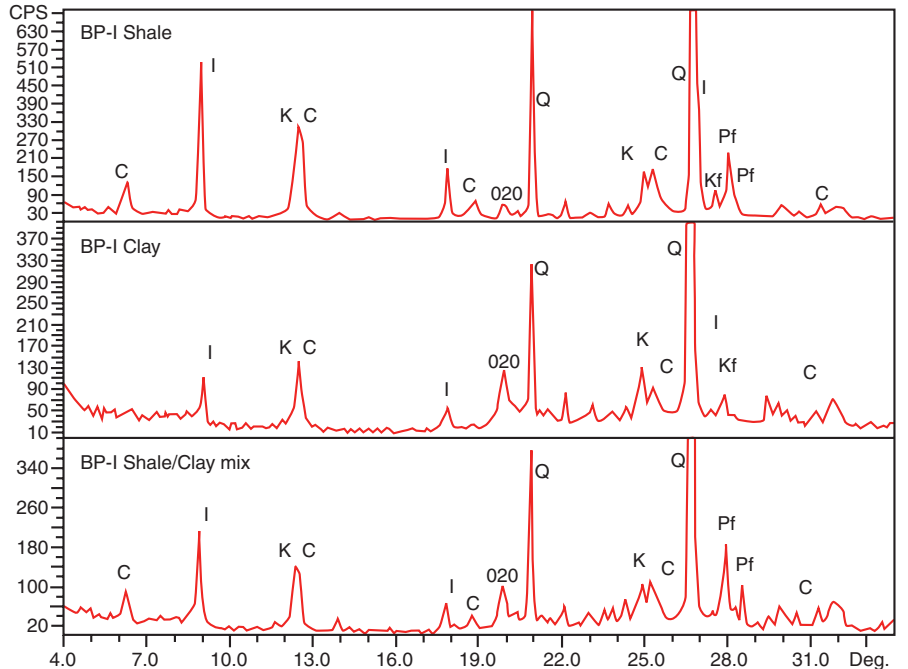


Figure 2 X-ray diffractograms of random bulk pack of Brick Plant 1 shale, clay, and clay and shale brick mix. The mineral peak indications are chlorite (C), illite (I), kaolinite (K), (020) peak (common to all clay minerals), quartz (Q), K-feldspar (Kf), and plagioclase feldspar (Pf). CPS, counts per second.

Table 7 Mineral composition (wt %) and clay index for the samples of fly ash, clay, and clay plus shale.¹

Sample	I	K	C	Kf	Pf	Cl	Q	M	Cc	Mg	H	Glass
Ponded fly ash						0	15	24	1.9	2.9	2.3	55
BP-I clay	38	15	7.6	0.4	2.7	0.61	36					
BP-I shale-clay mix	26	7.5	7.3	0.7	8.1	0.41	50					

¹I, illite; K, kaolinite; C, chlorite; Q, quartz; Kf, k-feldspar; Pf, plagioclase feldspar; Cl, clay index; M, mullite; Cc, calcite; Mg, magnetite; and H, hematite.

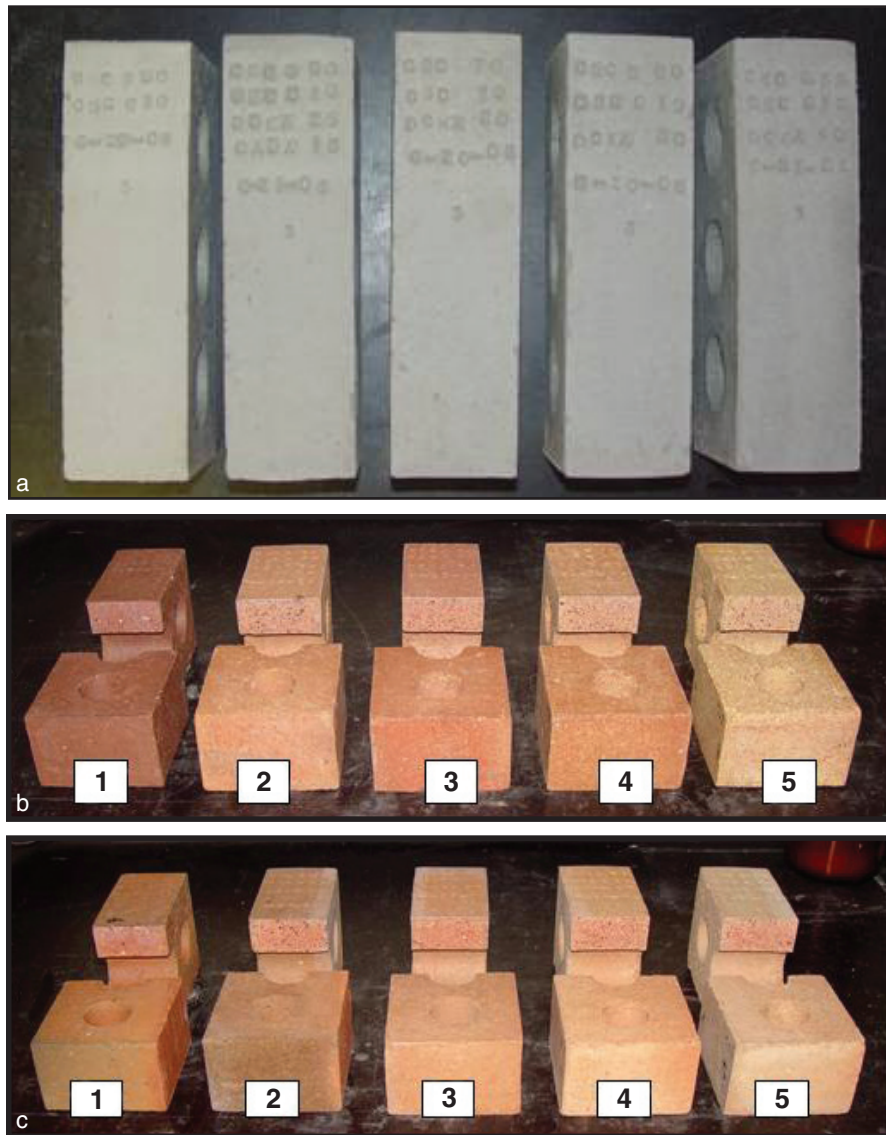


Figure 3 Full-size bricks (a) before firing (green bricks); (b) sawn in half, after firing at Brick Plant I; and (c) sawn in half, after firing at Brick Plant II.

Product Evaluation

Batch 1 Runs

Three full-size green building bricks were made for each formulation (Table 3). One set of five green bricks was fired

at the ISGS, and the other two sets were fired as parts of commercial firings at BP-I and BP-II. Figure 3a shows one set of the bricks before firing; Figure 3b shows the bricks fired at BP-I sawn in half for examination; Figure 3c shows

the bricks fired at BP-II sawn in half for examination.

The physical appearance of the fired bricks suggested that firings at BP-I and BP-II were successfully completed. The fired bricks were without scum, lime pops, cracks, black hearts, or red hearts. The bricks exhibited slight color differences, which varied depending on composition. Bricks were lighter in color as the weight percentage of RAW-1 in the formulation increased.

The total weight loss and shrinkage of the bricks after drying and firing are shown in Tables 8 and 9. The bricks made with RAW-1 (Bricks 2, 3, 4, and 5) lost more weight (22.8 to 32.1% at BP-I and 20.1 to 22.5% at BP-II) during drying and firing than did the reference standard formulation Brick 1 (15.8%). However, during drying and firing, bricks made with RAW-1 in the formulation (Bricks 2, 3, 4, and 5) shrank less (2.4% for the bricks fired by BP-I and 1.6 to 3.9% for the bricks fired by BP-II) than the reference standard Brick 1 (7.1% for the bricks fired by BP-I and 6.3% for the bricks fired by BP-II). These differences could be due to differences in firing method and tempera-

Table 8 Total weight loss and shrinkage for Batch 1 bricks fired at Brick Plant I.

Brick formulation	Total weight loss (%)	Total shrinkage (%)
1 ¹	15.8	7.1
2	24.9	2.4
3	22.8	2.4
4	25.4	2.4
5	32.1	2.4

¹Reference standard. Brick formulations are given in Table 3.

Table 9 Total weight loss and shrinkage for Batch 1 bricks fired at Brick Plant II.

Brick formulation	Total weight loss (%)	Total shrinkage (%)
1 ¹	15.8	6.3
2	22.5	2.4
3	20.1	3.9
4	20.5	3.1
5	22.5	1.6

¹Reference standard. Brick formulations are given in Table 3.

ture program. BP-I is equipped with a stationary kiln, and BP-II is equipped with a tunnel kiln.

The engineering properties of the Batch 1 fired bricks were determined. The fired bricks were sawn in half to test absorption and compressive strength tests according to ASTM method C67. Results are shown in Table 10 for the bricks fired at BP-I and in Table 11 for those fired at BP-II.

A distinct trend was observed for the cold water and boiling water absorption and compressive strength of the bricks fired at BP-I or BP-II (Tables 10 and 11). Bricks 2, 3, 4, and 5, which contained FGD-sulfite (RAW-1), absorbed more cold water (11.76% at BP-II to 23.58% at BP-I) than the reference standard brick (4.93% at BP-I to 6.91% at BP-II). The bricks containing FGD-sulfite also were softer (lower compressive strength) than the reference brick. Compressive strengths of Bricks 2, 3, 4, and 5 ranged from 1,481 at BP-1 to 3,415 psi at BP-2; the compressive strengths of the reference standard Brick 1 was 7,680 psi at BP-I and 7,353 psi at BP-II. The saturation coefficients of the bricks containing RAW-1 fired at BP-I ranged from 0.84 to 0.86, and those of the bricks fired at BP-II ranged from 0.77 to 0.85.

A general trend was observed for the compressive strength of the fired bricks containing RAW-1. As the concentration of RAW-1 in the bricks increased, the compressive strength decreased. However, Brick 2, containing 15% bottom ash and 25% RAW-1, showed about 1.1 to 2 times greater compressive strength than the bricks without bottom ash (Bricks 3, 4, and 5). The bricks containing FGD material, which were whiter and weaker, would be acceptable for use as specialty bricks in areas with warmer climates. The results of this study suggest that the engineering properties of

bricks containing FGD materials can be improved through the addition of bottom ash.

According to ASTM C62 specifications, Bricks 3, 4, and 5 (with 20, 30, and 40 wt% FGD-sulfite, respectively) fired at BP-I (Table 10) belong to the negligible-weathering grade, and Brick 2 (with 15% bottom ash) belongs to the moderate-weathering grade. For the bricks fired by BP-II (Table 11), Brick 5 belongs to the negligible-weathering grade, Bricks 3 and 4 belong to the moderate-weathering grade, and Brick 2 (with 15% bottom ash) belongs to the severe-weathering grade.

Results from our previous study (Chou et al. 2006a) showed that the engineering properties of the bricks made by mold pressing were significantly improved when commercial production used extrusion to form the green bricks. For example, the molded bricks from the study's bench-scale production had compressive strengths that ranged from 5,800 to 8,000 psi, whereas extruded bricks with the same feed formulation from the commercial-scale testing showed a compressive strength of 16,905 psi. If a similar ratio

is applied, the engineering properties of Batch 1 bricks formed by extrusion might be acceptable for use under moderate or severe weathering when produced by commercial methods.

Batch 2 Runs

The formulations for the Batch 2 runs are shown in Table 4. Firing of the test bricks was successfully completed at BP-1 during a normal commercial firing. The fired bricks were cut in half to examine color and other characteristics inside and outside the brick body and to prepare for the engineering property tests. Photographs of these sawn bricks are shown in Figure 4.

Brick Plant I found that the color and appearance of all their commercially fired Batch 2 bricks were acceptable. The bricks showed no cracks, lime pops, scum, black hearts, or red hearts. The bricks containing fly ash blended with bottom ash (Bricks 1, 2, 3, and 4) were similar in their red color to Brick 7, the reference standard brick made without CCBs.

In the Batch 1 runs, Bricks 2, 3, 4, and 5 containing FGD-sulfite from Utility

Table 10 Engineering properties of Batch 1 bricks fired at Brick Plant I.

Brick formulation ¹	Cold water absorption (wt%)	Boiling water absorption (wt%)	Saturation coefficient	Compressive strength (psi)	ASTM C62 classification ²
1 ³	4.93	6.88	0.72	7,680	SW
2	17.57	20.92	0.84	2,811	MW
3	16.40	19.30	0.85	2,143	NW
4	20.18	23.60	0.86	1,965	NW
5	23.58	27.97	0.84	1,481	NW

¹Brick formulations are given in Table 3.

²See Table 2 for complete information; SW, severe weathering; MW, moderate weathering; NW, negligible weathering.

³Reference standard.

Table 11 Engineering properties of Batch 1 bricks fired at Brick Plant II.

Brick formulation ¹	Cold water absorption (wt%)	Boiling water absorption (wt%)	Saturation coefficient	Compressive strength (psi)	ASTM C62 classification ²
1 ³	6.91	8.98	0.77	7,353	SW
2	12.72	16.33	0.78	3,415	SW
3	13.87	16.36	0.85	3,160	MW
4	11.76	15.05	0.78	2,374	MW
5	14.51	18.77	0.77	1,978	NW

¹Reference standard. Brick formulations are given in Table 3.

²See Table 2 for complete information; SW, severe weathering; MW, moderate weathering; NW, negligible weathering.

³Reference standard.



Figure 4 Full-size bricks, sawn in half, after firing at Brick Plant I. Brick 7 is the reference standard commercial formulation brick.

A (RAW-1) were much lighter in color than the bricks without FGD materials. However, in the Batch 2 runs, Bricks 5, 6, 8, 9, and 10 containing FGD-sulfite from Utility B or C had a red color similar to the reference standard brick (Brick 7). The amount of Fe_2O_3 in the feed material is generally the major factor determining the redness of the fired products. The redder color of the Batch 2 bricks could be due to the relatively small amount of added FGD CCBs (≤ 28.6 vol%; ≤ 12.8 wt%) compared with the 20 to 40 wt% added to the Batch 1 bricks. Therefore, the amounts of Fe_2O_3 in the feed for the Batch 2 bricks were less diluted by the FGD material.

The engineering properties of the Batch 2 fired bricks were measured. The data for water absorption, compressive strength, and ASTM C62 classification are shown in Table 12.

According to the ASTM C62 specifications (Table 2), the cold water absorption for the reference standard (Brick 7) and brick formulations 1 to 3 containing fly ash and bottom ash met the specified standard of less than 8 wt%; formulation 4, at 8.48 wt%, slightly exceeded the maximum allowed absorption (Table 12). This result indicated that addition of the FGD CCBs increased water absorption by the brick. The cold water absorption for bricks containing FGD CCBs

ranged from 11.55 to 13.00 wt%. All of the bricks had a maximum saturation coefficient of ≤ 0.78 and a compressive strength of greater than 3,000 psi, meeting the ASTM specification for building bricks of severe-weathering grade (ASTM 2005).

Environmental Assessment

To study the possible environmental impacts of using fired bricks containing CCBs, pulverized fired-brick samples made with optimized formulations for potential commercial production were subjected to a simulated acid rainwater extraction. Fired brick samples with feed formulations 4, 6, and 10 (Table 4) were chosen for these tests. Brick sample extracts were analyzed according to the U.S. EPA Method 1320 (U.S. Environmental Protection Agency 1986). Table 13 presents the concentrations of 20 elements in the extracts and the regulatory thresholds for these elements for acid extractions from comparable solid wastes. The concentrations of the elements of concern (having available U.S. EPA limits) in the extracts of these brick samples are well below the regulatory thresholds, which indicates that the fired bricks containing CCBs can be considered environmentally safe construction products.

Additionally, a set of the intermediate (green bricks) and final (fired) bricks were pulverized and analyzed for their chemical composition. As expected, all of the brick samples showed a major loss of carbon (measured as loss on ignition [LOI value]), sulfur, and mercury in the fired products (data not shown). A direct method for determining the amounts of sulfur and mercury that were released into the air during brick firing was beyond the scope of this investigation. The chemical composition tests on the raw materials, however, indicated that the bricks containing FGD materials had sulfur contents of 14.10 to 21.30% and mercury contents of 0.18 mg/kg to 0.44 mg/kg; the fly ash, bottom ash, clay, and shale samples all had sulfur contents of $\leq 0.57\%$ and mercury contents of ≤ 0.06 mg/kg (Table 5).

Based on the test results, the fired bricks with FGD materials had good

physical appearance and engineering properties. The U.S. EPA Method 1320 standards showed that these fired bricks could be considered environmentally safe construction products. However, further investigation is needed to determine whether the high sulfur concentration introduced to the bricks by the addition of FGD material poses an issue of secondary emission during brick firing.

Economic Assessment

This study assessed the economic feasibility of producing fired bricks with fly ash and bottom ash blended with clay and shale at BP-I. Because the existing machinery at BP-I could be used for production, there were no associated capital costs. The cost of obtaining the raw materials and the production costs were the two major economic factors affected by the raw material substitution.

Fly ash and bottom ash CCBs are readily available throughout the year. Power plants pay substantial amounts to dispose of their ash in landfills and holding ponds; consequently, the plants are eager to sell these by-products at little or no cost. In some cases, they are willing to financially assist a company that wants to use the ash. The main cost of the CCBs is transportation from the power plant to the brick plant.

To help quantify costs, as part of our study, a trucking company was contacted to estimate the cost of shipping ash from a specific utility plant to BP-I. Because the distance between the two locations was less than 5 miles, the trucking company estimated its charge at an hourly rate of \$65 rather than

charging per mile. The truck could carry 25 tons of ash, and a maximum time of 2 hours was thought to be needed for loading, transportation, and unloading the ash. With these constraints, the overall shipping cost was estimated at \$5.20/ton $[(\$65 \times 2)/25]$. However, if the utility plant were to incur half of the shipping cost, the transportation cost estimate would be \$2.60/ton for the brick company.

Using fly ash and bottom ash as substitute raw materials in bricks can reduce the annual consumption of clay and shale, thereby reducing the annual mining costs for BP-I. BP-I owns and operates mines to produce its clay and shale raw materials. According to its estimate, the cost of mining is \$127,000 annually (excluding depreciation costs). The shared cost of transporting fly ash and bottom ash from the util-

Table 12 Engineering properties of Batch 2 bricks fired at Brick Plant I.

Brick formulation ¹	Cold water absorption (wt%)	Boiling water absorption (wt%)	Saturation coefficient	Compressive strength (psi)	ASTM C62 classification ²
1	7.97	11.44	0.70	4,931	SW
2	6.29	9.76	0.64	4,048	SW
3	6.43	9.80	0.66	5,384	SW
4	8.48	12.23	0.69	3,934	SW
5	12.50	15.94	0.78	3,137	SW
6	13.00	17.67	0.74	3,538	SW
7 ³	3.47	5.76	0.60	5,854	SW
8	11.81	15.13	0.78	3,204	SW
9	11.55	15.07	0.77	3,962	SW
10	12.41	17.39	0.71	3,541	SW

¹Brick formulations are given in Table 3.

²See Table 2 for complete information; SW, severe weathering; MW, moderate weathering; NW, negligible weathering.

³Reference standard.

Table 13 Concentrations (mg/L) of elements in the extracts generated from simulated acid rainwater extractions.^{1,2}

Sample	Al ³	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe
Blank 1	<0.02	<0.001	<0.02	0.004	<0.1	<0.001	<0.001	<0.001	<0.001	<0.04
Blank 2	<0.02	<0.001	<0.02	0.003	<0.1	<0.001	<0.001	<0.001	<0.001	<0.04
Brick 4	0.09	0.007	0.57	0.069	57.0	<0.001	<0.001	<0.001	<0.001	1.21
Brick 6	0.08	0.008	0.72	0.069	57.0	<0.001	<0.001	0.036	<0.001	0.86
Brick 10	0.16	0.004	0.31	0.072	117.5	<0.001	<0.001	<0.001	<0.001	1.08
EPA limit	-	-	-	100	-	1.00	-	5.00	-	-

Sample	K	Li	Mg	Na	Ni	Pb	S	Se	Zn	Hg
Blank 1	<0.1	<0.001	<0.02	0.18	<0.001	<0.001	32	<0.001	<0.004	<0.00001
Blank 2	<0.1	<0.001	<0.02	0.21	<0.001	<0.001	29	<0.001	<0.004	<0.00001
Brick 4	1.40	0.087	3.85	7.00	0.007	<0.001	48	<0.001	<0.004	<0.00001
Brick 6	1.45	0.043	4.00	7.75	0.005	<0.001	46	<0.001	<0.004	<0.00001
Brick 10	2.05	0.051	2.35	7.10	0.004	<0.001	86	<0.001	<0.004	<0.00001
EPA limit	-	-	-	-	5.00	5.00	-	1.00	-	0.2

¹Solid to acidic water ratio, 1:20.

²Extracts from fired Bricks 4, 6, and 10 are identified in Table 4; Blanks 1 and 2 are values for the simulated acid rainwater before used for extraction.

³Al, aluminum; As, arsenic; B, boron; Ba, barium; Ca, calcium; Cd, cadmium; Co, cobalt; Cr, chromium; Cu, copper; Fe, iron; K, potassium; Li, lithium; Mg, magnesium; Na, sodium; Ni, nickel; Pb, lead; S, sulfur; Se, selenium; Zn, zinc; Hg, mercury.

ity plant to BP-I is \$2.60/ton. If BP-I uses a substitution formula of 20% fly ash, 20% bottom ash, and 60% clay and shale, the cost of transporting the ash would be \$26,520/year (12,000,000 bricks/year \times 4.25 lb/brick \times 1/2000 ton/lb \times 2.60 \$/ton \times 0.4 part ash). The savings in mining costs would be \$50,800/year (\$127,000 \times 0.4 part ash). The net cost savings would be \$24,280/year (\$50,800 – \$26,520), assuming no cost for ash.

During raw material processing, mined clay and shale must be crushed and extensively ground. Fly ash, a material with a fine particle size, does not require such procedures, which can reduce raw material costs in proportion to the amount of fly ash used. Conversely, bottom ash contains coarser particles and requires preparation similar to that of clay and shale. The cost of grinding raw materials at BP-I is \$75,000 annually (excluding depreciation costs). By using 20% fly ash, BP-I could be expected to save \$15,000/year (\$75,000 \times 0.2). The total cost savings for BP-I by using a feed formulation of 20% fly ash, 20% bottom ash, and 60% clay and shale for its brick production would be \$39,280/year.

Conclusions

Various combinations of fly ash, bottom ash, and FGD-sulfite and FGD-sulfate CCBs were used as a partial replacement for the shale that is generally mixed with clay to make fired bricks. Fired bricks made with these raw materials contained no scum, lime pops, cracks, black hearts, or red hearts. Engineering properties of the majority of these fired bricks met the ASTM classification for a severe-weathering grade brick, although some were suited only for moderate-weathering or negligible-weathering grade. Fired bricks made with fly ash and bottom ash blends were comparable in color to fired bricks without CCBs. Bricks containing substantial quantities of FGD-sulfite were lighter in color, lower in compressive strength, and greater in water absorption capacity than the reference standard fired bricks made without CCBs. The addition of bottom ash to the brick composition increased

brick redness, improved its compressive strength, and decreased its water absorption capacity.

Simulated acid rainwater extraction tests showed that all of the fired bricks containing CCBs produced in our tests, including those containing fly ash and bottom ash, can be considered environmentally safe construction products. The fly ash and bottom ash from our specific project source can be recommended for use in making fired bricks. However, to fully evaluate the environmental impact of using higher sulfur content FGD CCBs as an ingredient in fired bricks, further studies are warranted to determine the fate of the sulfur during brick firing.

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References

American Coal Ash Association, 2006, ACAA releases 2005 coal combustion products survey findings, September 29, 2006. <http://acaaffiniscape.com/associations/8003/files/2005%20CCP%20Survey%20%2809-19-06%29Corrected-11-09-07.pdf>.

ASTM C62, 2005, Standard specification for building brick—Solid masonry units made from clay or shale, *in* Annual book of ASTM standards: ASTM International. <http://www.astm.org/standards/index.shtml>.

ASTM C67-07, 2007, Standard test methods for sampling and testing brick and structural clay tile, *in* Annual book of ASTM standards: ASTM International. <http://www.astm.org/standards/index.shtml>.

Brick Industry Association, 2006, Manufacturing, classification, and selection of brick, Part 1: Technical notes on brick construction, technical note 9. <http://www.gobrick.com/BIA/technotes/t9.pdf>.

Chou, M.-I. M., S.-F. J. Chou, V. Patel, and J.W. Stucki, 2005. Commercial production of fired bricks with Illinois Basin Class F fly ash: Proceedings and oral presentation at the International Congress on Fly Ash Utilization, December 4–7, 2005, New Delhi, India, p. 1.

Chou, M.-I. M., S.-F. J. Chou, V. Patel, M. D. Pickering, and J.W. Stucki, 2006a, Manufacturing fired bricks with Class F fly ash from Illinois Basin coals: Final report (Project period: September 1, 2004 to August 31, 2006) to the DOE/WVU/SIUC Combustion Byproducts Recycling Consortium: Illinois State Geological Survey, 29 p.

Chou, M.-I. M., S.-F. J. Chou, M.D. Pickering, and J.W. Stucki, 2006b, An environmental assessment of fired bricks containing fly ash: Proceedings, Division of Fuel Chemistry, 232nd ACS National Meeting, San Francisco, CA, September 10–14, 2006.

Chou, M.-I., K. Ghiassi, J.M. Lytle, S.F. Chou, and D.D. Banerjee, 1998, Marketable ammonium sulfate fertilizer and fine calcium carbonate from FGD-gypsum: Proceedings Twenty-third International Technical Conference on Coal Utilization and Fuel System, Clearwater, FL, March 9–14, 1998.

U.S. Environmental Protection Agency, 1986, Method 1320—Multiple extraction procedure for solid waste: U.S. Government Printing Office, Washington, DC, Environmental Protection Agency, 4 p. <http://www.epa.gov/epawaste/hazard/test-methods/sw946/pdfs/1320.pdf>.

