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Coal Ash By-Product from Shanxi Province, China, for the Production of Portland–Calcium Sulfoaluminate

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A B S T R A C T

Twenty bulk samples were collected from ponded coal combustion ash in Shanxi Province, China, as part of an investigation of their beneficiation potential. The samples were shipped to the University of Kentucky, where they were chemically analyzed. The samples were highly consistent in chemistry, falling within the ASTM C-618 class F compositional range. The particle size of the ponded ash was relatively coarse, with only ~7% by weight on average, falling below 200 mesh (75 μm) particle size. The bulk of the material (>80%) was within 50 by 200 mesh (equivalent to 300 by 75 μm). X-ray diffraction investigation combined with microscopy indicated that the agglomeration was probably due to the presence of small amounts (i.e., ~3.5%) of gypsum. The utilization potential of the ash was assessed in light of its characteristics and location. The presence of sulfate and relatively high alumina concentration, which averaged ~37%, suggested that it may serve as an important ingredient in the fabrication of a Portland–calcium sulfoaluminate (CSA) hybrid cement. Portland-CSA hybrid clinkers were successfully produced from this ponded ash when mixed with hydrated lime, gypsum, fluorite, and bauxite. The raw mixture was fired at 1250°C for 60 minutes twice (sample D) and consisted of approximately 40% alite (C_3S), 21% belite (C_2S), 3% ferrite (brownmillerite or C_4AF), 32% CSA (ye'elimite, Klein's compound, or $C_4A_3SO_3$), and no free lime by weight.

A R T I C L E   I N F O

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1. Introduction

The Shentou coal ash originates from the 4 × 500-MW Shentou Second Power Plant, located in Shuozhou City, in the Shanxi Province, China. This power plant produces energy for large population centers in eastern China, and thus significant amounts of coal ash are produced and must be landfilled if no applications are found (Peltier, 2013).

The aims and objectives of this research were to chemically and physically characterize the Shentou coal ash and, from these preliminary results, identify ways to reuse, recycle, or do both with this ash. In particular, Shentou coal ash has been tested for use as raw material for the production of alite–calcium sulfoaluminate (CSA) clinker.

A total of 20 bagged samples were collected from the large storage pond of the Shentou power station ash (Figure 1) and shipped to the University of Kentucky Center for Applied Energy Research (CAER). Three sets of samples were collected, labeled A, B, and C, from each of the three major cells in the pond. These materials were repacked and riffle-split into subsamples for chemical and physical analyses. One sample was lost when its bag was torn open in transit. Additionally, a sample of the ash was collected directly from the power plant (D-1) and shipped via air freight.

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Fig. 1. Google Earth photo of large ash pond samples for study (approximately 2800 m width).

2. Characterization of the Shentou Coal Ash

2.1. Experimental procedures

The major and trace elements in the samples were quantified with X-ray fluorescence (XRF) analyses. The procedure followed ASTM D4326-13 standard (ASTM International, 2013a) and was performed in a PW 2404 X-ray spectrometer supplied by Thermo Scientific Philips (Waltham, PA).

Loss on ignition was performed on all samples following the ASTM C7348-13 standard (ASTM International, 2013b).

All X-ray diffraction (XRD) analyses were performed with a Philips X'Pert diffractometer (model PW3040-PRO) operating at 45 kV and 40 mA and utilizing Cu K-α radiation. Before analyses, the samples were mechanically ground in a small shatter box and, if necessary, were also ground by hand with a ceramic mortar and pestle. The samples were dry mounted in aluminum holders. Samples for qualitative XRD were front loaded. The step size was set at 0.017° at 0.035°/s, over 8° to 60° 2θ. All of the XRD analyses used a 0.5° fixed antiscatter slit and a fixed divergence slit of 0.25°. The qualitative XRD analyses utilized 0.02 rad Soller slits and a diffracted antiscatter slit of 5.0 mm. For qualitative XRD, the crystalline phases were identified with an International Centre for Diffraction Data (Newton Square, PA) powder diffraction database.

The determination of particle size distribution was performed on each dry sample by sieving them twice through sieve sizes 50, 100, and 200 mesh, equivalent to 250, 150, and 75 μm, respectively.

Light microscope images of Kentucky average ash and Shentou ashes were captured with a Leica M205 C (Leica Microsystems, Buffalo Grove, IL). Additionally, scanning electron microscopy (SEM) images were taken of only the small fraction (below 75 μm) of each ash. Samples were placed on carbon tape and loaded into the Hitachi S-4800 SEM. SEM analyses were performed at 5 kV and 10 nA for dry and ponded Shentou ash.

2.2. Results

2.2.1. Chemical composition

Chemical analyses were performed on all the ash pond samples (Tables 1 and 2), and the samples were found to be very similar to

Table 1
Major oxide composition of Shentou ash pond samples, a dry sample from the power plant (D-1), and the average Kentucky ash (K07)

	Oxide composition (wt%)										
ID	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	TiO_2	SO_3	Sum
Shentou ash pond samples											
A-1	47.17	38.92	4.17	3.88	0.62	0.05	0.48	0.13	1.14	1.83	98.39
A-3	47.18	39.11	4.33	3.94	0.62	0.05	0.49	0.14	1.18	1.61	98.65
A-4	47.19	39.03	4.72	3.61	0.61	0.06	0.50	0.13	1.18	1.46	98.49
A-5	47.20	38.75	4.75	4.03	0.61	0.05	0.48	0.14	1.16	1.67	98.84
A-6	47.21	38.93	4.75	3.60	0.63	0.05	0.49	0.13	1.20	1.40	98.39
A-7	47.22	38.88	4.48	3.80	0.61	0.05	0.49	0.13	1.17	1.59	98.42
B-1	47.23	35.78	5.56	4.43	0.66	0.05	0.51	0.13	1.10	1.98	97.43
B-2	47.24	35.84	5.03	4.56	0.65	0.05	0.52	0.13	1.11	2.31	97.44
B-3	47.25	36.11	4.90	4.37	0.66	0.05	0.50	0.13	1.09	2.18	97.24
B-4	47.26	35.45	5.23	4.52	0.63	0.05	0.52	0.13	1.11	2.25	97.15
B-5	47.27	35.98	5.09	4.49	0.64	0.04	0.52	0.13	1.12	2.14	97.42
B-6	47.28	36.08	4.95	4.63	0.65	0.05	0.53	0.13	1.12	2.34	97.76
B-7	47.29	35.84	5.30	4.55	0.64	0.05	0.52	0.13	1.12	2.12	97.56
B-8	47.30	35.71	5.21	4.55	0.64	0.04	0.51	0.13	1.11	2.07	97.27
C-1	47.31	36.96	4.39	4.50	0.66	0.04	0.57	0.13	1.12	2.59	98.27
C-2	47.32	37.26	4.36	4.37	0.66	0.05	0.58	0.12	1.13	2.50	98.35
C-3	47.33	36.80	4.38	4.37	0.65	0.04	0.57	0.12	1.12	2.52	97.90
C-4	47.34	36.87	4.28	4.37	0.67	0.05	0.57	0.13	1.14	2.50	97.92
C-5	47.35	36.63	4.57	4.42	0.67	0.05	0.57	0.13	1.14	2.47	98.00
Mean	47.26	37.10	4.76	4.26	0.64	0.05	0.52	0.13	1.13	2.08	97.94
STD	0.06	1.37	0.40	0.34	0.02	0.01	0.03	0.00	0.03	0.39	0.53
CV (%)	0.1	3.7	8.4	7.9	3.1	10.4	6.5	3.6	2.7	18.5	0.54
Shentou dry sample											
D-1	47.18	41.11	4.35	2.87	0.68	0.03	0.49	0.24	1.46	0.10	98.51
K07	50.49	24.65	13.41	3.80	1.12	0.58	2.51	0.28	1.23	1.31	99.38

Note: STD = standard deviation; CV = coefficient of variation for ash pond samples only; K07 = average composition of 170 samples of all types of fly ash collected in Kentucky in 2007.

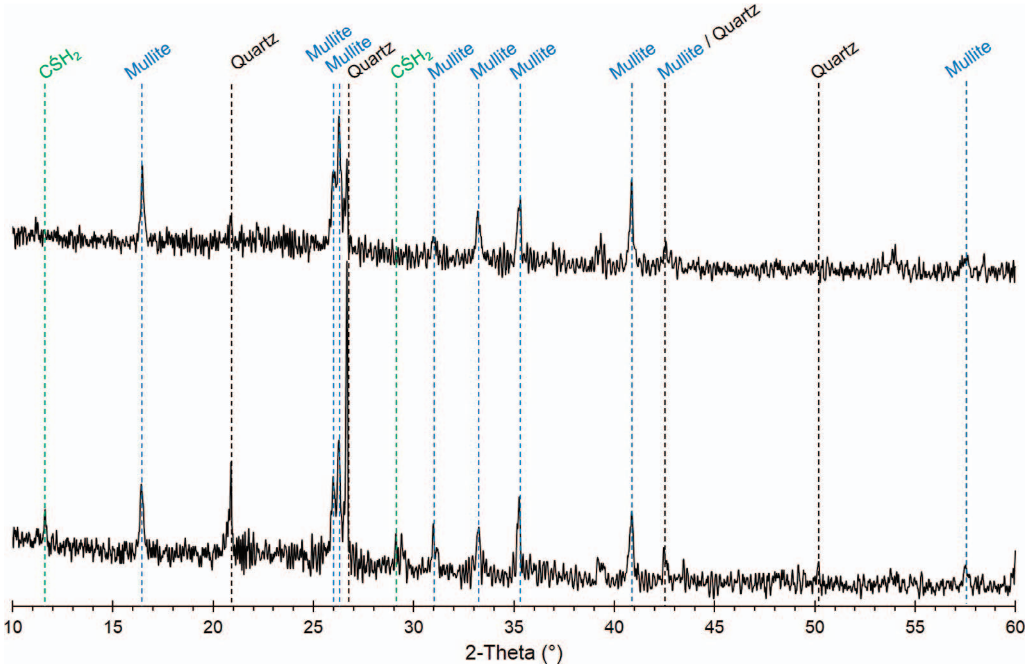

Fig. 2. X-ray diffraction patterns of dry (D-1) and ponded (B2) Shentou ash.

each other in composition. In addition to these major elements (Table 1), the Shentou ash contained a small amount of carbon (~2 wt%). Because the calcium oxide content was low (below 10% by weight) and the total (SiO_2+Al_2O_3+Fe_2O_3) content was above 70% by weight, this ash is defined as a class F fly ash according to ASTM C618-12 (ASTM International, 2012). For comparison, the average composition of 170 samples of all types of fly ash collected in Kentucky in 2007 (K07) are presented in the Tables 1 and 2 (Hower et al., 2009). The major difference is the higher level of Al_2O_3 and a lower level of Fe_2O_3 in the Shentou ash.

In general, the Shentou ponded ash contained lower concentrations of trace elements compared with the Kentucky average ash (K07). Of particular note was As, which was 100 times less than K07. Conversely, a few trace elements such as Mo, Rb, and Zr were higher in the Shentou ash. This is a reflection of the different locations of the source coals for the ash.

2.2.2. *Powder X-ray diffraction*

Powder XRD analyses on the Shentou samples revealed that the ponded ash contained quartz, mullite, and gypsum (Figure 2), and the dry Shentou ash contained quartz and mullite but no gypsum. Mullite (approximately $Al_6Si_2O_{13}$) is a common mineral in class F fly ash and readily forms from alumina and silica at high temperature. Its abundance is reflective of the high alumina content of this ash. The slightly curved background of the XRD diffractogram, as shown in Figure 2, suggests the presence of some amorphous materials.

2.2.3. *Particle size distribution*

The Shentou ash pond samples were found to be much coarser than the ash samples from Kentucky or the as-received dry sample from the power plant. Most of the ponded ash is in the size range of 75–300 μm (82%), whereas the dry ash was mostly less than 150 μm (89%) (Table 3). Both were very coarse compared with the Kentucky average ash, which is mostly (89%) less than 75 μm. The cause for the comparative coarseness of the Shentou ponded ash is not known, but the agglomeration of particles via solution and precipitation of gypsum in the pond is suspected. Scrubber materials are also stored in the ash ponds, and the ponded ash is significantly higher (~2.0% vs. 0.1%) in SO_3 than the dry received ash (Table 1), which lends credence to this hypothesis.

2.2.4. *Particle size appearance*

Microscopic images of samples from the ponded Shentou ash are shown in Figure 3, along with images of ponded ash from the Tennessee Valley Authority ash pond at Kingston, TN. The Kingston ash (Figure 3a) is well rounded, whereas the ponded Shentou ash in Figures 3b and 3c had an abundance of irregularly shaped particles that do not appear to be fully fused, in addition to fused glassy particles. This may be due to the high alumina content of this ash, which would result in a very high melting temperature or possibly pulverizer conditions. For the fine ash (below 75 μm) analyzed by SEM, the Kingston ponded ash was also well rounded, as shown in Figure 3e. The dry and ponded Shentou ashes, in Figures 3f and 3g, were agglomerated and significantly coarser.

2.3. *Shentou ash utilization*

All characterization analyses defined the Shentou ash as a class F fly ash composed of quartz, mullite, and amorphous materials; gypsum was in the pond sample. The important advantage of this material was chemical composition consistency and quality, which could be very useful as a raw material in CSA cement. From microscopic and SEM images, dry and ponded Shentou ashes were both very coarse, with irregular shaped particles, which would not be suitable for use as a pozzolanic material.

Furthermore, because of the presence of gypsum, this material may not be suitable as an aggregate. However, because of its high alumina content, this material was very suitable as raw material for the fabrication of alite-CSA clinkers, which is discussed in Section 3.

Table 2
Trace elements in the composition of Shentou ash pond samples, a dry power plant sample (D-1), and Kentucky average ash (K07)

	Trace elements (wt ppm)															
ID	As	Ba	Cd	Co	Cr	Cu	Mo	Mn	Ni	Pb	Rb	Sb	Sr	V	Zn	Zr
Shentou ash pond samples																
A-1	<1	228	<1	8	60	17	171	171	12	42	276	3	391	140	32	290
A-3	<1	240	<1	12	56	15	184	174	13	40	270	4	458	154	32	317
A-4	<1	250	<1	7	65	18	177	178	16	38	275	3	431	152	32	317
A-5	<1	245	<1	9	60	17	191	181	14	36	272	5	481	145	30	327
A-6	<1	262	<1	7	69	16	146	180	15	42	278	1	379	150	37	293
A-7	<1	256	<1	9	69	15	196	175	18	38	269	5	464	148	31	325
B-1	<1	230	<1	11	74	21	122	204	26	47	224	1	327	131	44	283
B-2	<1	230	<1	16	68	18	166	192	25	38	262	4	392	131	36	309
B-3	<1	223	<1	11	61	18	107	191	14	51	234	<1	290	125	47	260
B-4	<1	230	<1	13	77	22	189	198	18	33	268	6	424	127	35	328
B-5	<1	221	<1	9	60	16	173	193	14	38	254	4	402	133	34	317
B-6	<1	227	<1	9	59	17	185	189	13	36	258	5	430	133	35	328
B-7	<1	223	<1	11	64	17	178	196	16	40	231	5	419	133	33	326
B-8	<1	222	<1	9	62	16	179	195	14	35	262	5	410	129	33	323
C-1	<1	216	<1	9	60	15	191	200	13	35	283	5	416	138	34	318
C-2	<1	230	<1	8	63	15	184	197	14	36	284	4	402	138	34	313
C-3	<1	228	<1	9	66	16	189	194	15	39	260	5	409	137	33	316
C-4	<1	241	<1	10	60	14	191	191	15	41	255	5	419	137	35	323
C-5	<1	238	<1	11	67	17	188	199	23	39	254	5	438	139	39	331
Mean	<1	234	<1	10	64	17	174	189	16	39	262	4	410	138	35	313
STD		12		2	5	2	24	10	4	4	17	1	44	8	4	19
CV (%)		5		22	8	12	14	5	25	11	6	33	11	6	12	6
Shentou dry sample																
D-1	7	482	<1	10	81	34	196	197	20	53	218	4	832	240	72	35
K07	106	1139	<1	42	153	193	103	242	156	64	28	5	1045	589	309	97

Note: STD = standard deviation; CV = coefficient of variation for ash pond samples only; K07 = average composition of 170 samples of all types of fly ash collected in Kentucky in 2007.

3. Synthesis of Alite-CSA Clinker

3.1. Materials and procedures

3.1.1. Materials

The materials used in the fabrication of the clinkers include the ponded Shentou coal ash (sample A-3), whose characterization results were previously discussed, and materials intended for the production of several samples of alite-CSA clinkers, which are presented in Table 4: hydrated lime, flue gas desulfurization (FGD) gypsum, bauxite, and calcium fluorite (reagent chemical supplied by Sigma-Aldrich). Kentucky average ash K07 is listed for comparison with the Shentou ash and is described in Sections 2 and 3.

Table 3
Particle size distributions of ponded and dry Shentou ash samples and Kentucky average ash

	Distribution (%)				
			Ponded Shentou ash		
Particle size (μm)	Kentucky ash (K07)	Dry Shentou ash	Avg	Min	Max
>300	1	0	7	2	17
300 by 150	2	10	43	29	64
150 by 75	8	30	39	27	55
<75	89	59	11	3	17

Note: K07 = average composition of 170 samples of all types of fly ash collected in Kentucky in 2007; Avg = average; Min = minimum; Max = maximum.

3.1.2. Production of clinker samples

Small samples of clinkers were produced (Section 3.1) by first mixing all the weighted materials in a mortar and pestle until completely homogenized. Deionized water was added to the homogenized mixture at 10% by weight (1 g for 10 g of materials) and mixed to produce 28 × 7-mm pellets pressed under approximately 110 kN of load, which were then placed in an oven at 60°C for 4 hours. This water-to-solids ratio of 10% was chosen to create well-compacted pellets. The small pellets were placed in a platinum crucible and fired at 800°C for 30 minutes, followed by firing at temperatures of 1250°C or 1275°C for 60 or 120 minutes. This firing regime was chosen to obtain the clinker phases desired: ye'elimite and alite. Indeed, alite starts to form at 1300°C, and ye'elimite starts to decompose at 1300–1350°C (Taylor, 1997; Guo and Xie, 2011). A firing temperature just below 1300°C was thus selected. All pellets were quenched in air, crushed in a shatter box for 45 seconds, and placed in a desiccator until powder XRD/Rietveld analyses were performed.

3.1.3. Characterization methods

The chemical composition of the samples were quantified by XRF analysis, as described in Section 2.1.

All XRD analyses were performed with a Philips X'Pert diffractometer (model PW3040-PRO) operating at 45 kV and 40 mA and utilizing Cu K-α radiation. Rietveld analysis of XRD diffractrograms was used to determine the weight percent concentrations of crystalline phases in very fine grained samples of clinker samples. Before analyses, the samples were mechanically ground in a small shatter

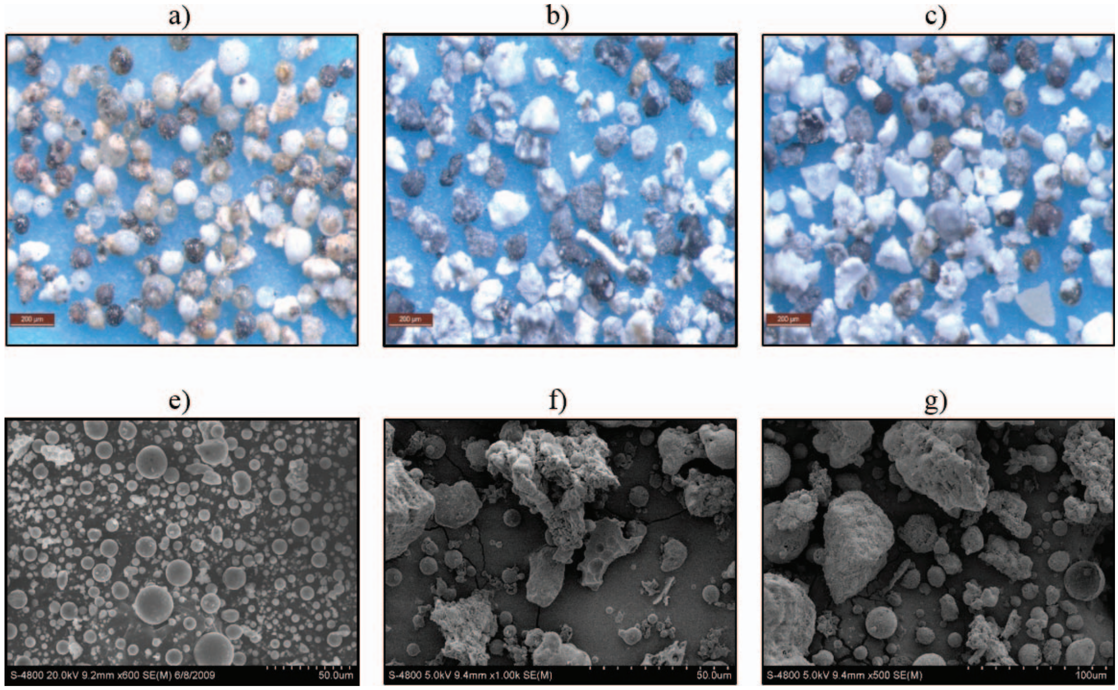

Fig. 3. Light microscope images with an approximately 1620-μm width of (a) Tennessee Valley Authority Kingston ponded ash, (b) dry Shentou ash, (c) ponded Shentou ash. (The scale bar is 200 μm.) Scanning electron microscope images of ash below 75 μm of (e) Kingston ponded ash (~210-μm width), (f) dry Shentou ash (approximately 125-μm width), (g) ponded Shentou ash (~250-μm width).

box, and if necessary were also ground by hand with a ceramic mortar and pestle. The samples were dry mounted in aluminum holders. Samples for Rietveld analyses were back-loaded, where the method is described in Appendix B3 of the User's Guide (PANalytical, 2005). The step size for Rietveld analyses was 0.017° at 0.013°/s, over 8–90° 2θ. All of the XRD analyses used a 0.5° fixed antiscatter slit and a fixed divergence slit of 0.25°. The Rietveld analyses used 0.04 rad Soller slits and a diffracted antiscatter slit of 5.5 mm. Philips PANalytical X'Pert computer software was used for the Rietveld refinements. The phases were modeled with either crystallographic information taken from the literature or from files included in the PANalytical Rietveld software. All phases were refined for scale factors, and phases in concentrations at and above 2.0 wt% were also refined for lattice parameters (a, b, c, α, β, and γ, as warranted) and preferred orientation. On the basis of visual inspection of the diffractogram results and intensity difference plots, phases at concentrations above 10.0 wt% were usually refined for the peak width parameter *W* and, as warranted, for the peak width parameters *U* and *V*, peak shape and asymmetry.

3.2. Composition of alite-CSA clinkers

Alite-CSA cement is a hybrid of Portland and CSA cements, composed of alite (C_3S) and CSA ($C_4A_3\acute{S}$, where $\acute{S}$ is SO_3); these elements are usually incompatible because of their conflicting formation/decomposition temperatures. Both phases have recognized advantages in their respective cement composition. Alite is the most important contributor of strength and performance in ordinary Portland cement and hydrates rapidly to form calcium silicate hydrates (C-S-H, where C is CaO, S is SiO_2, and H is H_2O). CSA is the most important phase in CSA cements because it contributes to most of the early strength development by hydrating to ettringite ($C_3A\cdot3C\acute{S}\cdot32H$, where A is Al_2O_3) if enough calcium sulfate is present; otherwise, monosulfate will form (Winnefeld and Lothenbach, 2010). The combination of both phases into one hybrid cement creates a material able to gain early (a few hours) and late (a few weeks or months) strength from both clinker phases of alite and CSA. However, the production of such a cement is not straightforward because of the formation temperature incompatibility of both clinker phases: CSA

Table 4
Chemical compositions of materials used for the preparation of alite–calcium sulfoaluminate clinkers, the Kentucky's ash average (K07), and the Shentou ash's average

	Chemical composition (wt%)											
Material	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	LOI	MgO	K_2O	Na_2O	P_2O_5	TiO_2	Sum
Hydrated lime	65.27	1.96	1.56	0.42	0.07	29.83	2.11	0.07	0.11	0.01	0.07	101.48
FGD gypsum	32.31	1.03	0.22	0.08	45.86	20.78	0.17	0.03	0.02	0.01	0.08	100.59
Fluorite	Considered pure CaF2 as reagent chemical											
Shentou A3	3.81	45.63	37.83	4.19	1.56	3.24	0.60	0.47	0.05	0.14	1.14	98.65
Bauxite	0.16	6.64	58.54	6.28	0.24	27.60	0.20	0.01	0.01	0.22	2.18	102.07
K07	3.8	50.49	24.65	13.41	1.31	NA	1.12	2.51	0.58	0.28	1.23	99.38
Average Shentou ash	4.26	47.26	37.10	4.76	2.08	NA	0.64	0.52	0.05	0.13	1.13	97.94

Note: NA = not available; LOI = loss on ignition; FGD = flue gas desulfurization; K07 = average composition of 170 samples of all types of fly ash collected in Kentucky in 2007.

Table 5
Rietveld analyses of A, B, C, and D clinkers fired at various firing regimes

		Samples				
		A	B	C	Theoretical clinker	D[1]
Firing temperature (°C)		1250	1250	1275		1250 bis
Dwell time (min)		60	120	60		60 bis
Clinker composition (wt%)						
C_3S		38.8	34.6	40.0	≈60	40.2
C_2S		21.0	21.0	18.5	–	21.3
C_4AF		5.4	6.3	4.6	≈6	3.2
$C_4A_3\acute{S}$		28.8	30.3	29.9	≈30	32.0
$C\acute{S}$		–	–	–	≈0.6	2.0
f_{CaO}		–	–	–	–	–
C_3A		–	1.3	3.7	–	–
MgO		1.4	1.6	1.5	–	1.2
Mayenite		1.1	1.8	–	–	–
Portlandite		1.6	3.1	1.8	–	–
$C_{11}A_7 \cdot CaF_2$		1.9	–	–	–	–
Rietveld parameters						
R values	Rexp	3.56	3.83	3.52		3.52
	Rp	5.29	6.62	5.66		5.35
	Rwp	7.30	8.49	7.80		7.24
GOF		4.21	4.91	4.90		4.24

Note: S = SiO_2; A = Al_2O_3; F = Fe_2O_3; $\acute{S}$ = SO_3; f_{CaO} = free lime; Rexp = expected pattern residual error; Rp = profile pattern residual error; Rwp = weighted pattern residual error; GOF = goodness of fit.
[1] Sample D is sample A fired twice at 1250°C with a dwell time of 60 minutes for each firing.

starts to form at 900°C and decomposes at 1300–1350°C (Guo and Xie, 2011), whereas alite starts to form at 1300°C (Taylor, 1997). The use of fluxes and mineralizers such as calcium fluorite and calcium sulfate are thus needed to produce an intermediate phase, called fluorellestadite (Blanco-Varela et al., 1986, 1995; Gimenez-Molina and Blanco-Varela, 1995). Studies have been published on the influence of both mineralizers and fluxes, as well as the establishment of specific clinker parameters (Duvallet, 2014; Duvallet et al., 2014; Robl et al., 2015).

The fabrication of alite-CSA cement requires raw materials rich in silica, calcium, alumina, and sulfate. The calcium and sulfate elements can easily be found in limestone, hydrated lime, and gypsum. The Shentou fly ash is a source of both silica and alumina. By using equations established by Zhou and discussed in Robl et al. (2015), a specific composition has been determined (65.5 wt% hydrated lime, 6.3 wt% FGD gypsum, 0.7 wt% fluorite, 22.5 wt% Shentou A3, and 5.0 wt% bauxite; Table 4) to optimize and maximize the amounts of alite and CSA phases. This composition has a theoretical clinker composition of approximately 60% C_3S, 6% C_4AF (where F is Fe_2O_3), 30% $C_4A_3\acute{S}$, and 0.6% $C\acute{S}$ by weight (Table 5).

The pellets were fired at 1250°C or 1275°C for 60 or 120 minutes, and the clinker compositions are shown in Table 5. Samples A, B, and C fired at 1250°C for 60 minutes, 1250°C for 120 minutes, and 1275°C for 60 minutes, respectively, all show free lime in their XRD patterns in Figure 4.

Samples A and C were fired for 60 minutes at 1250°C and 1275°C, respectively, and both samples contained noticeable amounts of uncombined free lime as CaO, as shown in the diffractograms in Figure 4. Some tricalcium aluminate (C_3A), produced from the decomposition of calcium sulfoaluminate ($C_4A_3\acute{S}$), was present in samples B and C, because of the long dwell time for sample B and the high firing temperature of 1275°C for sample C (Table 5).

Sample D was produced by regrinding and refiring sample A at 1250°C for 60 minutes. Visual inspections of the XRD patterns indicated that the free lime concentration was reduced after refiring (Figure 4). As expected, C_3S, C_2S, and $C_4A_3\acute{S}$ are major phases in all four samples.

Rietveld analyses were performed on samples A, B, C, and D to quantify the primary phases as shown in Table 5. The presence of

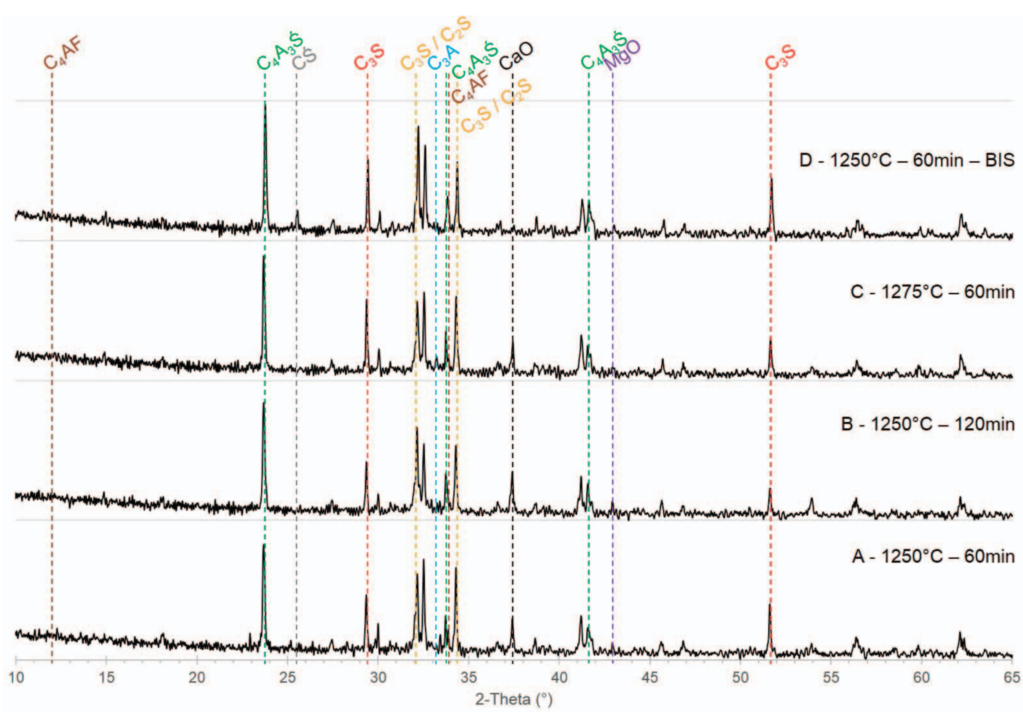

Fig. 4. Powder X-ray diffraction patterns of samples A–D. Lime (CaO) reacted and disappeared in the formation of clinker D, as shown by the disappearance of the peak at 37.4° 2θ with Cu K-α radiation.

portlandite was detected in samples A, B, and C (Table 5) at concentrations of 1.6, 3.1, and 1.8 wt%, respectively. Rietveld analyses were performed a few months after the XRD analyses. Despite storage in a desiccator, the presence of portlandite suggests that the original free lime in the ash hydrated. Additionally, no portlandite was present in sample D, which confirms the absence of free lime observed in Figure 4. These analyses also confirmed the presence of tricalcium aluminate with a long dwell time of 120 minutes and an increase in temperature from 1250°C to 1275°C, which meant that the CSA was decomposing. The clinker composition, referred to as sample D, was richer in alite and CSA than sample A. Both C_3S and $C_4A_3\acute{S}$ amounts were closer to the theoretical values, and the second firing process significantly reduced the quantity of free lime.

As a result, both a high firing temperature of 1275°C or a long dwell time of 120 minutes affected the clinker composition of the samples negatively because tricalcium aluminate formed as a result of the decomposition of ye'elimite. The firing regime of 1250°C with a dwell time of 60 minutes was optimum, because of the absence of tricalcium aluminate; however, some free lime was still present. A regrinding and refiring of sample A, also called sample D, led to a clinker with no more free lime.

4. Conclusions

Shentou coal ash from the Shanxi Province, China, was characterized through various methods and was then classified as a class F fly ash. The chemical composition was consistent within all of the Shentou pond samples and had high quality. The ponded Shentou ash contained quartz, mullite, and gypsum, whereas the dry ash only contained quartz and mullite. The ponded Shentou ash (82 wt% in the size range of 75–300 μm) was coarser than the dry ash (89 wt%, below 150 μm in size); both ponded and dry ashes were physically made of irregular shaped particles. Based on these data and on the high concentration of alumina and silica in the ash, Shentou coal ash was utilized as raw material for the production of alite-CSA clinkers. Finally, the production of hybrid alite-CSA clinkers with Shentou ash as a major component was demonstrated to be feasible. A clinker composed of approximately 40 wt% C_3S, 21 wt% C_2S, 3 wt% C_4AF, 32 wt% $C_4A_3\acute{S}$, 2 wt% $C\acute{S}$, and 1.2 wt% MgO was produced by firing the sample twice at 1250°C for 60 minutes, with crushing of the clinker in a shatter box between the two firing procedures.

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