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Chemistry of coal and coal combustion products from Kentucky power plants: Results from the 2007 sampling, with emphasis on selenium

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ABSTRACT

Kentucky produced over 8 Mt of coal combustion products (CCPs) in 2006, with 30% of the CCPs being utilized, a significant increase from our 1996 and 2001 surveys. As much of the increase is related to increased utilization of flue-gas desulfurization (FGD) gypsum, the increased production of FGD gypsum coincident with the commissioning of new FGD units and the saturation of the (currently) weak market for new construction, the percentage of utilization may decrease by the time of the next planned survey (2011).

The concentration of volatile trace elements in the feed coal and in the pulverizer reject, while associated with pyritic sulfur, are somewhat independent of the pyritic sulfur content owing to provincial variations in the trace element content of coal minerals. Consequently, high-pyrite/high-S coals do not necessarily produce the highest-As, -Se, and -Hg (among other elements) fly ashes. Among the power plants in Kentucky, plants with intermediate sulfur contents have some of the highest concentrations of volatile trace elements in their fly ashes. In general, volatile trace elements in fly ash increase in concentration from the first through to the last row of the pollution control system owing to the decrease in flue gas temperature and decrease in particle size (and increase in surface area) in that direction. Mercury is dependent upon the carbon content in addition to the flue gas temperature. Selenium is more problematical, showing no consistent trend within the ash collection systems.

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1. Introduction

The distribution and natural capture of hazardous elements by coal-combustion fly ash has been of concern in recent years. In particular, the capture of Hg by fly ash carbons is of interest because of its potential to complement or offset more-expensive engineered solutions. Mercury capture is a function of the flue gas temperature at the collection point (Hower et al., 1999, 2000a, 2005a; Sakulpitakphon et al., 2000, 2003; Mardon and Hower,

2004; Mastalerz et al., 2004); the amount of fly ash carbon (Hower et al., 2000b; Maroto-Valer et al., 2001); and the form of fly ash carbon, including the rank of the feed coal (Hower et al., 2000b; Maroto-Valer et al., 2002; Külaots et al., 2004; Goodarzi, 2005; Goodarzi et al., 2006; Suárez-Ruiz et al., 2007; Suárez-Ruiz and Parra, 2007; Hower et al., 2008b); in addition to variations in the amount of Hg in the feed coal. Many other volatile trace elements, such as Zn and As, are known to increase in concentration towards the cooler back rows of the electrostatic precipitator (ESP) array (Hower et al., 1999; Sakulpitakphon et al., 2003; Mardon et al., 2008; Depoi et al., 2008; Levandowski and Kalkreuth, 2009; Meij and te Winkel, 2009). Fly ash particles are also finer in the last ESP

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Table 1

Production and sales percentage of fly ash, bottom ash and slag, FGD sulfite, and FGD gypsum from Kentucky utility power plants for selected years from 1978 to 2006.

Year	MW Rating	Fly Ash Production (Mt)	% Sold	Slag/Bottom Ash Production (Mt)	% Sold
2006	15000	3.098	11.4%	1.283	47.5%
2001	15000	3.414	3.6%	1.213	36.3%
1996	15240	3.237	4.0%	1.081	42.6%
1991	16000	2.519	4.8%	1.386	52.7%
1978	11500	2.807		1.424	

Year	FGD Gypsum (Mt)	% Sold	FGD Sulfite (Mt)	% Sold	Total Production (Mt)	% Sold
2006	2.245	78.1%	1.466	0.3%	8.092	30.1%
2001	1.979	61.5%	2.070	0.0%	8.676	20.5%
1996	1.498	11.2%	1.707	0.0%	7.523	10.1%
1991	0.617	0.0%	1.997	0.0%	6.519	13.0%
1978	na		na		4.231	

rows, contributing to a greater surface area for element condensation.¹ Less is known about the distribution of Se in pollution-control systems. We have conducted several studies of the distribution of Se and other trace elements. This contribution, based on the 2007 iteration of our pentannual survey of Kentucky power plants, follows those investigations with further studies of the distribution of Se and other trace elements in power plant feed coals and the resulting fly ashes.

Hower and Robertson (2004) found unusual Se concentrations in one fly ash fraction from the cyclone fly ash from the combustion of a 1:1 western US bituminous: Powder River Basin subbituminous coal blend and ~1–2% tire-derived fuel. While Se was only 12 µg/g (whole-sample basis) in the feed coal, the element was substantially enriched (260 µg/g) in one sample from the first row ESP fly ash from unit 2 (of the two units studied). The source of the Se could not be determined, although sulfides (such as pyrite) and selenides in coal (such as clausthalite; not observed in the feed coal, however) can be sources of Se. It is not known if the tire-derived fuel could have contributed substantial Se to the blend. In any case, the unusual concentration on one side of the Unit 2 first-row ESP could not be fully explained.

Mardon and Hower (2004) studied the chemistry of a single-seam/single-mine coal and the consequent fly ash in a November 2001 sampling at a 220-MW eastern Kentucky power plant (plant I in this and previous studies of Kentucky power plants). Selenium determination was made by hydride-generation atomic absorption spectrometry at the US Geological Survey laboratories in Denver, CO (O'Leary, 1997). The delivered high volatile A bituminous coal and the pulverized feed both had 4 µg/g Se (whole-sample basis). In contrast to As, another volatile element, Se concentration peaked in the first row of the ESP, averaging over 155 µg/g, followed by a drop in concentration to about 9 µg/g in the second ESP row and less than 6 µg/g in the third ESP row. Based on the rule-of-thumb assumption that each ESP row captures 80% of the fly ash reaching that row, nearly 99% of the Se captured by the ESP fly ashes was in the first-row ESP ash. Selenium does not follow the trend of As, since only 74% of the As is captured by the first-row ESP fly ash. Neither does Se follow the trend of Hg which was dictated by both fly ash C and flue-gas temperature.

¹Note that we are primarily referring to the surface area of the inorganic particles, generally dominated by glass. The fly ash carbons are also finer in the last ESP row versus the first ESP row, but their surface area is a function of the porosity, not simply the area of the outer particle surface.

López-Antón et al. (2006) found that high-Ca ashes tended to have a strong tendency towards Se capture. Narukawa et al. (2005) conducted sequential extraction studies of various fly ashes, with an emphasis on the speciation of As, Se, and Sb. The sources of the fly ash were not named, but were noted as coming from several countries. Selenium ranged from 2.26 to 5.15 µg/g in the fly ashes. Selenium was found to be in an exchangeable, Se(IV), form or, in one fly ash, bound to the fly ash carbon. Forms bound to carbonates or Fe-Mn oxides (spinel) were not detected. Residual Se bound to the silicate (glass) fraction was also present. The percentage of water-soluble Se, determined after 8 h of leaching, was very similar to the amount of exchangeable Se. The absence of carbonate-bound Se in the Narukawa et al. (2005) study is not a contradiction to López-Antón et al. (2006) since, in the latter case, the equilibrium Se form was predicted to be CaSe, not a carbonate. Agnihotri et al. (1998) noted selenate and selenite forms in their Se-sorption experiments. López-Antón et al. (2006) did not find Se to be bound to fly ash carbon, in agreement with five of the six ashes studied by Narukawa et al. (2005). Li et al. (2006) also noted a Ca association in their study of the removal of SO₂ and Se from flue gas. As with the modeling conducted by Urban and Wilcox (2006a, b), they noted that the actual determination of Se in flue gas is difficult due to its extremely low concentration.

In this study, we discuss both the trends of coal combustion product (CCP) production at Kentucky power plants and the results of the geochemical investigations of coal and CCP samples from the 2007 sample collection.

2. Methods

Samples analyzed for this study were collected as part of a 2007 survey of all utility coal-fired power plants in Kentucky with additional consideration of samples collected in the 2002 survey (Hower et al., 2005a). The pentannual power plant surveys at the CAER consist of both an information survey (section 3.1) and a collection of coal, fly ash, bottom ash, and, where appropriate, FGD products at most of the utility units in Kentucky.

Selenium had not yet been analyzed at the time of the writing of latter paper. Additional samples were collected at three of the same power plants in 2004 (plants E, H, and I; as coded in previous studies).

Coal quality analyses of coal collected for the survey was done at the Center for Applied Energy Research (CAER). Proximate, ultimate, heating value, and sulfur forms analysis were conducted following the appropriate ASTM procedures. Ash chemistry was

Table 2

a/ Summary of proximate and ultimate analyses (% , as-received basis), forms of sulfur (% , as-received basis), heating value (Megajoules/kg, as-received basis), and Chlorine (ppm, as-received basis) for pulverized coals and pulverizer rejects from 2007 sampling of Kentucky power plants. b/ Summary of major oxides (% , ash basis) for pulverized coals and pulverizer rejects from 2007 sampling of Kentucky power plants. c/ Summary of minor elements (ppm on ash basis for all except Hg on whole-coal basis) for pulverized coals and pulverizer rejects from 2007 sampling of Kentucky power plants.

Table 2a																	
%S feed																	
coal	type		Ash	Moisture	VM	FC	C	H	N	O	S	S _{py}	S _{sulf}	S _{org}	HV	Cl	
<1	pulv coal	<i>ave.</i>	11.77	2.62	34.46	51.15	71.35	5.00	1.33	9.73	0.82	0.14	0.07	0.61	29.18	1134	
		<i>s.d.</i>	1.26	1.87	2.10	3.18	3.05	0.17	0.09	3.46	0.14	0.09	0.11	0.10	1.32	555	
		<i>count</i>	7	7	7	7	7	7	7	7	7	7	7	7	7	6	7
		<i>max</i>	13.64	6.81	38.71	53.50	74.44	5.31	1.51	17.25	0.94	0.25	0.29	0.68	30.27	1633	
		<i>min</i>	10.01	1.63	32.34	44.47	65.65	4.82	1.25	7.42	0.53	0.02	0.01	0.38	26.76	113	
<1	reject	<i>ave.</i>	28.61	1.64	31.86	37.89	55.78	3.90	1.06	6.53	4.12	3.34	0.07	0.71	23.68	705	
		<i>s.d.</i>	9.48	0.42	2.52	8.16	9.37	0.68	0.27	1.88	2.75	2.40	0.08	0.54	4.05	458	
		<i>count</i>	8	8	8	8	8	8	8	8	8	8	8	8	7	8	
		<i>max</i>	39.60	2.32	35.43	47.35	67.34	4.77	1.38	8.47	9.03	7.18	0.24	1.61	28.36	1202	
		<i>min</i>	16.70	1.22	27.94	25.66	43.69	3.12	0.67	3.08	1.54	0.69	0.01	0.12	17.75	51	
1 to 2	pulv coal	<i>ave.</i>	11.48	1.94	35.74	50.85	71.74	5.05	1.46	8.84	1.43	0.58	0.04	0.82	29.79	947	
		<i>s.d.</i>	1.82	0.12	0.46	1.46	1.68	0.08	0.11	0.44	0.22	0.29	0.02	0.22	0.72	472	
		<i>count</i>	6	6	6	6	6	6	6	6	6	6	5	6	6	6	
		<i>max</i>	13.18	2.11	36.50	53.33	74.85	5.16	1.59	9.29	1.59	0.89	0.07	1.25	31.03	1894	
		<i>min</i>	8.14	1.80	35.05	49.13	70.26	4.96	1.33	8.22	1.03	0.21	0.01	0.65	29.11	632	
1 to 2	reject	<i>ave.</i>	42.06	1.02	29.81	25.88	36.30	2.64	0.67	5.88	19.28	17.97	0.13	1.38	20.73	643	
		<i>s.d.</i>	19.41	0.54	5.10	14.79	24.00	1.69	0.48	2.40	15.34	15.41	0.07	1.40	6.18	610	
		<i>count</i>	7	7	7	7	7	7	7	3	7	7	7	6	5	5	
		<i>max</i>	66.41	1.75	36.18	46.25	68.46	4.87	1.34	7.39	38.91	38.67	0.23	3.39	28.58	1672	
		<i>min</i>	16.11	0.31	24.18	9.10	6.74	0.59	0.07	3.11	2.08	1.49	0.02	0.05	15.15	125	
2 to 3	pulv coal	<i>ave.</i>	10.26	4.99	36.33	48.43	68.10	5.16	1.34	12.30	2.84	1.17	0.20	1.47	28.46	673	
		<i>s.d.</i>	2.47	1.66	0.54	1.29	1.10	0.22	0.10	1.69	0.14	0.22	0.17	0.16	0.56	136	
		<i>count</i>	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
		<i>max</i>	13.20	7.10	37.23	50.18	69.72	5.46	1.45	14.59	2.93	1.52	0.45	1.67	29.27	814	
		<i>min</i>	6.36	3.28	35.85	47.17	66.89	4.89	1.25	9.97	2.59	1.03	0.02	1.30	27.77	526	
2 to 3	reject	<i>ave.</i>	49.34	1.65	29.57	19.44	25.24	1.98	0.51	9.72	30.48	26.51	0.26	3.72	22.73	277	
		<i>s.d.</i>	24.40	1.90	4.83	17.88	26.11	1.99	0.60		15.24	15.88	0.21	3.71	5.80	199	
		<i>count</i>	5	5	5	5	5	5	5	1	5	5	5	5	2	2	
		<i>max</i>	69.41	4.86	37.05	44.38	63.27	4.99	1.38		41.54	40.30	0.63	8.30	26.82	418	
		<i>min</i>	13.71	0.38	25.11	4.87	6.35	0.57	0.05		6.93	5.11	0.13	0.39	18.63	136	
>3	pulv coal	<i>ave.</i>	11.87	3.75	35.16	49.22	68.28	4.94	1.29	10.27	3.34	1.32	0.14	1.92	28.43	765	
		<i>s.d.</i>	1.06	1.41	4.37	4.35	1.49	0.29	0.05	1.91	0.19	0.20	0.17	0.27	0.73	636	
		<i>count</i>	8	8	8	8	8	8	8	8	8	8	6	8	8	7	
		<i>max</i>	13.55	6.19	38.20	56.89	69.90	5.26	1.35	14.10	3.73	1.53	0.47	2.33	29.41	1576	
		<i>min</i>	10.86	2.42	26.77	45.63	65.34	4.40	1.20	8.44	3.17	0.93	0.01	1.64	27.24	5	
>3	reject	<i>ave.</i>	64.13	0.57	26.41	8.89	9.15	0.78	0.14		40.60	36.31	0.25	4.04			
		<i>s.d.</i>	3.33	0.33	1.09	3.14	5.12	0.41	0.11		7.32	6.14	0.20	3.25			
		<i>count</i>	8	8	8	8	8	8	8	8	8	8	8	8			
		<i>max</i>	69.21	1.13	27.84	14.27	20.12	1.68	0.35		51.09	41.81	0.55	8.80			
		<i>min</i>	59.94	0.31	24.66	5.13	4.90	0.44	0.04		26.02	22.42	0.07	0.05			

Table 2b												
%S feed												
coal	type		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	SO ₃
<1	pulv coal	<i>ave.</i>	54.60	28.14	6.51	2.25	1.12	0.62	2.47	0.21	1.39	1.93
		<i>s.d.</i>	3.14	3.22	2.13	1.97	0.49	0.67	0.71	0.15	0.22	2.14
		<i>count</i>	7	7	7	7	7	7	7	7	7	7
		<i>max</i>	57.14	31.63	11.23	6.65	2.20	1.98	3.16	0.44	1.50	6.69
		<i>min</i>	47.98	21.59	5.02	0.84	0.75	0.19	0.96	0.10	0.89	0.47
<1	reject	<i>ave.</i>	50.25	15.57	23.14	3.88	1.03	0.27	1.45	0.25	0.95	4.21
		<i>s.d.</i>	11.18	6.23	11.97	2.54	0.51	0.32	0.49	0.11	0.25	3.12
		<i>count</i>	8	8	8	8	8	8	8	8	8	8
		<i>max</i>	64.05	25.52	42.49	9.37	1.76	1.06	2.09	0.48	1.34	10.22
		<i>min</i>	34.54	8.08	9.22	1.54	0.41	0.11	0.77	0.10	0.51	1.00
1 to 2	pulv coal	<i>ave.</i>	52.98	29.24	10.17	1.24	0.93	0.20	2.65	0.26	1.40	0.72
		<i>s.d.</i>	1.63	1.72	1.73	0.30	0.11	0.12	0.22	0.09	0.09	0.38
		<i>count</i>	6	6	6	6	6	6	6	6	6	6
		<i>max</i>	55.28	32.62	12.01	1.77	1.10	0.45	2.94	0.38	1.56	1.29
		<i>min</i>	50.35	27.79	7.26	0.99	0.80	0.13	2.38	0.17	1.31	0.16

Table 2.—Continued.

%S feed coal	type		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	SO ₃	
1 to 2	reject	<i>ave.</i>	30.41	10.98	46.56	4.61	1.40	0.10	1.17	0.13	0.75	4.44	
		<i>s.d.</i>	11.45	6.80	25.64	7.29	2.24	0.05	0.42	0.07	0.31	6.73	
		<i>count</i>	7	7	7	7	7	7	7	7	7	7	7
		<i>max</i>	48.43	20.59	74.69	20.42	6.34	0.18	1.90	0.21	1.23	18.20	
		<i>min</i>	17.94	4.01	15.71	0.48	0.13	0.05	0.61	0.04	0.43	0.49	
2 to 3	pulv coal	<i>ave.</i>	48.04	20.50	20.37	3.12	0.90	0.51	2.46	0.18	1.07	3.29	
		<i>s.d.</i>	3.86	2.93	4.58	0.42	0.15	0.19	0.38	0.03	0.07	0.66	
		<i>count</i>	5	5	5	5	5	5	5	5	5	5	5
		<i>max</i>	52.93	25.42	27.44	3.50	1.06	0.71	2.84	0.23	1.18	3.86	
		<i>min</i>	43.94	17.77	14.80	2.44	0.71	0.20	2.06	0.14	1.02	2.22	
2 to 3	reject	<i>ave.</i>	23.69	7.63	55.88	3.96	0.59	0.32	0.91	0.28	0.52	5.49	
		<i>s.d.</i>	15.59	6.45	20.02	1.44	0.48	0.26	0.77	0.26	0.34	4.72	
		<i>count</i>	5	5	5	5	5	5	5	5	5	5	5
		<i>max</i>	44.32	18.03	75.79	6.23	1.36	0.58	2.14	0.73	1.07	13.71	
		<i>min</i>	8.32	2.24	26.71	2.43	0.14	0.04	0.27	0.10	0.23	2.17	
>3	pulv coal	<i>ave.</i>	47.81	20.16	18.09	4.37	0.96	0.39	2.75	0.28	0.99	5.18	
		<i>s.d.</i>	2.45	1.16	2.60	1.55	0.11	0.11	0.38	0.08	0.07	2.69	
		<i>count</i>	8	8	8	8	8	8	8	8	8	8	8
		<i>max</i>	50.49	21.89	20.98	7.49	1.09	0.55	3.24	0.34	1.14	11.21	
		<i>min</i>	42.74	17.79	14.69	2.10	0.79	0.23	2.11	0.10	0.94	1.91	
>3	reject	<i>ave.</i>	13.13	3.86	70.31	4.34	0.34	0.30	0.55	0.48	0.33	5.38	
		<i>s.d.</i>	6.12	2.16	11.15	2.03	0.25	0.21	0.43	0.35	0.09	2.46	
		<i>count</i>	8	8	8	8	8	8	8	8	8	8	8
		<i>max</i>	26.55	8.82	85.34	6.91	0.72	0.69	1.57	1.11	0.52	8.16	
		<i>min</i>	7.04	1.77	48.28	0.85	0.08	0.05	0.21	0.05	0.24	1.34	

Table 2c

%S feed coal	type		Se	Hg	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Zr	Mo	Cd	Sb	Ba	Pb	
<1	pulv coal	<i>ave.</i>	5.86	0.08	341	125	217	27	150	298	184	40	19	1395	34	160	1	2	1216	59	
		<i>s.d.</i>	2.11	0.03	90	26	73	2	36	87	33	6	13	779	15	69	0	2	678	10	
		<i>count</i>	7	7	7	7	7	7	7	7	7	7	7	2	7	7	7	7	5	7	7
		<i>max</i>	7.94	0.14	405	148	317	31	216	426	251	50	28	2882	48	243	1	5	2721	67	
		<i>min</i>	1.51	0.05	147	70	122	24	114	154	151	34	9	825	1	70	1	1	736	38	
<1	reject	<i>ave.</i>	9.67	0.72	162	186	1057	62	58	88	250	199	12	590	121	110	1	7	655	71	
		<i>s.d.</i>	5.00	0.55	66	203	1177	28	28	90	431	144		413	69	42	0	4	436	31	
		<i>count</i>	8	8	8	8	8	8	8	8	7	6	8	1	7	8	4	8	8	8	8
		<i>max</i>	19.04	1.60	278	688	3670	103	93	215	1128	505		1132	201	170	1	12	1679	124	
		<i>min</i>	6.05	0.24	64	90	213	30	13	10	23	66		57	29	74	1	1	313	27	
1 to 2	pulv coal	<i>ave.</i>	4.97	0.11	385	140	146	37	119	254	149	99		1401	53	157	1	2	992	73	
		<i>s.d.</i>	1.49	0.05	35	3	31	4	16	53	36	52		503	6	39	0	1	71	19	
		<i>count</i>	5	6	6	6	6	6	6	6	6	6		6	5	6	6	6	6	6	
		<i>max</i>	6.24	0.19	442	144	204	41	139	341	214	183		2424	60	208	1	3	1060	103	
		<i>min</i>	2.75	0.03	334	136	120	29	94	198	112	52		1142	47	112	1	1	909	55	
1 to 2	reject	<i>ave.</i>	27.21	2.12	128	138	405	121	40	471	37	879	29	414	203	44	1	12	422	177	
		<i>s.d.</i>	30.17	1.57	82	37	167	65	22	640	26	830		348	59	0	4	181	163		
		<i>count</i>	7	7	7	7	7	7	6	2	2	7	1	3	7	1	7	7	7	7	
		<i>max</i>	71.00	3.85	263	168	603	194	69	923	55	2211		780	264	2	17	641	440		
		<i>min</i>	3.23	0.23	33	58	170	34	11	18	18	198		88	104	1	6	60	27		
2 to 3	pulv coal	<i>ave.</i>	3.27	0.11	427	170	252	52	142	89	399	93		263	131	71	1	5	442	45	
		<i>s.d.</i>	1.25	0.04	97	51	17	8	41	99	206	34		71	7	51	0	1	70	8	
		<i>count</i>	5	5	5	4	4	4	4	4	4	4		4	4	4	4	4	4	4	
		<i>max</i>	5.26	0.15	561	242	268	61	183	237	645	124		357	139	144	1	6	510	51	
		<i>min</i>	2.21	0.05	317	123	229	41	85	29	146	58		191	123	29	1	4	357	36	
2 to 3	reject	<i>ave.</i>	37.79	1.44	129	165	321	144	48		169	250		234	231	4	2	16	478	32	
		<i>s.d.</i>	41.26	0.70	149	40	46	50	42		182	48			50	1	5	168	29		
		<i>count</i>	5	5	5	4	4	4	4		2	4		1	4	1	4	4	4	4	
		<i>max</i>	89.00	2.19	377	210	387	183	108		297	310			263	2	21	610	72		
		<i>min</i>	2.90	0.41	31	112	282	74	12		40	199			157	1	9	245	4		

Table 2.—Continued.

Table 2c																					
%S feed coal	type		Se	Hg	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Zr	Mo	Cd	Sb	Ba	Pb	
>3	pulv coal	<i>ave.</i>	4.03	0.09	810	165	275	50	198	187	257	66		258	142	48	1	6	759	33	
		<i>s.d.</i>	3.09	0.04	1046	45	57	7	242	362	180	28		137	11	24	0	1	315	8	
		<i>count</i>	8	8	8	8	8	8	8	8	7	8	8		8	8	8	8	8	8	8
		<i>max</i>	10.97	0.14	3041	259	396	59	699	1006	645	107		519	163	83	1	8	1176	43	
		<i>min</i>	2.01	0.05	200	100	226	41	54	22	121	28		27	124	4	1	5	296	22	
>3	reject	<i>ave.</i>	49.80	1.75	48	168	454	173	39		159	233			258		2	19	504	29	
		<i>s.d.</i>	35.17	0.47	25	20	352	30	13		195	120			13		0	5	253	28	
		<i>count</i>	8	8	8	8	8	8	8		2	8			8		8	8	8	4	
		<i>max</i>	85.00	2.44	100	202	1313	209	64		297	451			271		2	26	1039	62	
		<i>min</i>	8.22	0.89	25	144	255	115	23			21	112			231		1	13	228	5

analyzed by x-ray fluorescence on a Phillips PW2404 x-ray spectrometer following procedures outlined by Hower and Bland (1989). Selenium was analyzed on whole-coal or whole-fly ash pressed pellets on the latter instrument. Mercury was analyzed with a LECO AMA254 Advanced Mercury Analyzer, an absorption spectrometer technique.

3. Discussion

3.1 CCB utilization trends

Coal combustion product production in Kentucky has exceeded 8 Mt in the last two survey years, 2001 and 2006, of the CAER's CCB utilization survey (utilization information is for the year prior to the coal and ash collection year; Table 1). A decrease from 2001 to 2006 is seen in the drop in fly ash and FGD sulfite production. The decrease in fly ash production might be attributed to the use of lower ash coals in 2006 than in the previous sampling. The decrease in FGD sulfite production is somewhat offset by the increase in FGD gypsum, representing a switch to forced oxidation of the FGD product in order to produce a marketable product and also the late-2006 commissioning of a gypsum-producing flue-gas desulfurization operation at a western Kentucky power plant. In the latter case, the gypsum is not currently marketed. Overall, increases in the amounts of gypsum, fly ash, and bottom ash and slag sales led to an increase in 2006 CCB sales to over 30% of production. The 10% increases in sales seen in each of the past two five-year intervals might not be sustained for the next planned survey in 2011. An increase in FGD capacity, as dictated by provisions of the U.S. Environmental Protection Agency's Clean Air Interstate Rule (2005), will mean that gypsum supplies will outstrip demand in the region. Based on the implementation of the EPA regulations and on known construction of FGD and CFBC units, Kentucky's installed SO₂-control technology is projected to increase from slightly over 50% of MW capacity in 2006 to over 70% of MW capacity in 2011. Complicating predictions is the overturning of the Clean Air Interstate Rule and the Clean Air Mercury Rule by the United States Court of Appeals District of Columbia Circuit (2008a, b) and the February 2009 decision by the Obama administration's Department of Justice to not pursue appeals of the rulings, instead drafting new rules (US EPA, 2009). Some utilities are proceeding with planned construction of FGD units, while others will wait for clarification of the regulations.

3.2 Pulverized coal and pulverizer rejects

Pulverization at the power plant both produces the feed coal size consist suitable for injection into the boiler and serves as a final pre-combustion step in removing hazardous trace elements from the boiler feed. Hower (2008) summarized the petrographic aspects of coal pulverization and that discussion will not be repeated here. Pulverization rejects a small amount of the feed coal, generally less than 1% of the input. Even at a small percent, such a rejection can account for a diversion of >10% of the hazardous elements from the boiler feed (Mardon and Hower, 2004; Hower et al., 2005a, 2006).

The chemistry of the 2007 pulverized coal and pulverizer reject samples are summarized, as grouped by the total sulfur content of the pulverized coal on Table 2 and the complete coal and coal combustion product data set is provided in Appendix Table A1. For comparison, the chemistry of the same sample types from studies in 2002 (previously discussed by Hower et al., 2005a) and 2004 (unpublished), combined with the 2007 data, are shown on Table 3 with the 2002 and 2004 coal and coal combustion product data provided in Appendix Table A2. The most obvious trend within both tables is the increase in total and pyritic S towards the high-S feed coals. While inherent in the design of the table for the pulverized coals (the groups are determined in 1%-S increments); it does not necessarily follow that the pulverizer rejects should show a similar increase. In both cases, there is an increase in pulverizer reject total and pyritic S from the low-S to the high-S group. In the case of the entire 2002–2007 population, the increase from the 2–3%-S to the >3%-S groups is much smaller than the increase from the 1–2%-S to 2–3%-S groups. The pulverized coal and pulverizer reject samples, while derived from the same feed coal, are independent samples. The individual characteristics of the feed coals, such as the type of pyrite present (finely dispersed framboidal forms versus more easily separated massive or cleat-filling forms), would play an important part in the separation between the pulverizer products.

As noted above, an important benefit of coal pulverization and the rejection of the oversize material is the elimination of a portion of the trace element stream from the boiler fuel. The pulverizer reject consistently has a higher percentage of Fe₂O₃ and CaO and a lower percentage of SiO₂ and Al₂O₃ than the pulverized feed coal. Accompanying this is a greater proportion of (generally) volatile siderophile trace elements in the pulverizer reject. Within the feed

Table 3

a/ Summary of proximate and ultimate analyses (% , as-received basis), forms of sulfur (% , as-received basis), heating value (Megajoules/kg, as-received basis), and Chlorine (ppm, as-received basis) for pulverized coals and pulverizer rejects from 2002, 2004, and 2007 samplings of Kentucky power plants. b/ Summary of major oxides (% , ash basis) for pulverized coals and pulverizer rejects from 2002, 2004, and 2007 samplings of Kentucky power plants. c/ Summary of minor elements (ppm on ash basis for all except Hg on whole-coal basis) for pulverized coals and pulverizer rejects from 2002, 2004, and 2007 samplings of Kentucky power plants.

%S feed			Ash	Moisture	C	H	N	O	S	S _{py}	S _{sulf}	S _{org}	HV	Cl	
coal	type	sample													
<1	pulv coal	<i>ave.</i>	11.44	2.62	71.72	5.05	1.32	9.71	0.76	0.15	0.03	0.58	29.41	816	
		<i>s.d.</i>	0.82	1.90	2.93	0.13	0.09	3.49	0.15	0.08	0.05	0.11	1.32	743	
		<i>count</i>	7	7	7	7	7	7	7	7	7	7	6	7	
		<i>max</i>	12.36	6.81	74.44	5.31	1.51	17.25	0.94	0.25	0.15	0.68	30.27	1633	
		<i>min</i>	10.01	1.35	65.65	4.91	1.25	7.42	0.53	0.02	0.01	0.38	26.76	0	
<1	reject	<i>ave.</i>	33.88	1.48	51.58	3.58	0.95	5.96	4.05	3.34	0.07	0.71	23.68	705	
		<i>s.d.</i>	16.48	0.52	14.87	1.08	0.37	2.10	2.63	2.40	0.08	0.54	4.05	458	
		<i>count</i>	10	10	10	10	10	10	10	10	8	8	8	7	8
		<i>max</i>	73.74	2.32	67.34	4.77	1.38	8.47	9.03	7.18	0.24	1.61	28.36	1202	
		<i>min</i>	16.70	0.55	16.49	1.03	0.16	2.69	1.54	0.69	0.01	0.12	17.75	51	
1 to 2	pulv coal	<i>ave.</i>	12.06	2.40	70.99	5.11	1.46	8.99	1.39	0.55	0.04	0.79	29.39	517	
		<i>s.d.</i>	2.25	0.42	2.50	0.14	0.09	0.83	0.25	0.21	0.04	0.18	1.05	597	
		<i>count</i>	16	16	16	16	16	16	16	15	14	15	14	11	
		<i>max</i>	16.86	3.26	74.85	5.36	1.59	11.79	1.77	0.89	0.15	1.25	31.03	1894	
		<i>min</i>	8.14	1.80	66.84	4.89	1.29	8.16	0.93	0.21	0.01	0.59	27.41	0	
1 to 2	reject	<i>ave.</i>	40.81	1.34	37.99	2.80	0.72	4.96	16.39	13.58	0.17	1.87	21.45	536	
		<i>s.d.</i>	16.64	0.63	21.47	1.56	0.45	1.84	12.06	13.00	0.19	1.27	5.50	605	
		<i>count</i>	17	14	17	17	17	11	17	12	12	11	9	6	
		<i>max</i>	66.41	2.41	68.46	4.90	1.34	7.39	38.91	38.67	0.55	3.39	28.58	1672	
		<i>min</i>	16.11	0.31	6.74	0.58	0.07	1.98	2.08	1.45	0.01	0.05	15.15	0	
2 to 3	pulv coal	<i>ave.</i>	11.55	3.74	68.94	5.11	1.47	10.42	2.50	1.21	0.20	1.42	29.24	663	
		<i>s.d.</i>	2.60	1.95	1.32	0.19	0.16	2.65	0.47	0.23	0.20	0.14	1.34	155	
		<i>count</i>	7	7	7	7	7	7	7	4	4	4	7	4	
		<i>max</i>	13.99	7.10	70.26	5.46	1.64	14.59	2.93	1.52	0.45	1.61	31.18	814	
		<i>min</i>	6.36	2.15	66.89	4.89	1.27	7.87	1.69	1.03	0.02	1.30	27.77	526	
2 to 3	reject	<i>ave.</i>	54.73	1.40	19.08	1.54	0.37	9.72	32.90	29.47	0.29	2.57	26.82	418	
		<i>s.d.</i>	23.14	1.94	24.77	1.93	0.57		14.73	16.67	0.23	3.10			
		<i>count</i>	5	5	5	5	5	1	5	4	4	4	1	1	
		<i>max</i>	69.41	4.86	63.27	4.99	1.38	9.72	41.54	40.30	0.63	7.15		418	
		<i>min</i>	13.71	0.38	6.35	0.57	0.05	9.72	6.93	5.11	0.13	0.39		418	
>3	pulv coal	<i>ave.</i>	11.64	3.21	69.50	5.00	1.33	8.84	3.67	1.41	0.12	2.15	28.99	383	
		<i>s.d.</i>	1.33	1.45	2.44	0.34	0.12	2.38	0.43	0.40	0.11	0.37	1.02	587	
		<i>count</i>	17	17	17	17	17	17	17	17	15	17	17	14	
		<i>max</i>	14.54	6.19	73.73	5.52	1.64	14.10	4.57	2.23	0.47	2.90	30.82	1576	
		<i>min</i>	9.53	1.12	65.34	4.27	1.17	5.69	3.17	0.89	0.01	1.64	27.24	0	
>3	reject	<i>ave.</i>	62.87	0.70	10.94	0.92	0.17	3.04	33.73	32.10	0.26	2.91	16.99	0	
		<i>s.d.</i>	6.41	0.61	8.98	0.75	0.18	2.00	10.40	10.15	0.21	2.93		0	
		<i>count</i>	17	17	17	17	17	3	17	13	13	13	1	3	
		<i>max</i>	70.84	2.61	40.08	3.34	0.74	5.32	51.09	41.81	0.65	8.80		0	
		<i>min</i>	43.22	0.16	3.34	0.30	0.04	1.58	7.30	4.98	0.02	0.05		0	

Table 3b

%S feed			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	SO ₃
coal	type	sample										
<1	pulv coal	<i>ave.</i>	55.41	28.04	6.50	2.15	1.14	0.69	2.36	0.21	1.46	1.75
		<i>s.d.</i>	3.37	3.13	2.12	2.01	0.49	0.64	0.64	0.16	0.28	2.20
		<i>count</i>	7	7	7	7	7	7	7	7	7	7
		<i>max</i>	57.68	31.63	11.23	6.65	2.20	1.98	2.81	0.44	1.76	6.69
		<i>min</i>	47.98	21.59	5.02	0.84	0.75	0.19	0.96	0.09	0.89	0.47
<1	reject	<i>ave.</i>	48.76	14.53	21.54	5.86	1.42	0.25	1.39	0.22	0.93	5.19
		<i>s.d.</i>	10.48	5.98	11.62	4.90	0.96	0.29	0.45	0.12	0.24	3.49
		<i>count</i>	10	10	10	10	10	10	10	10	10	10
		<i>max</i>	64.05	25.52	42.49	16.49	3.22	1.06	2.09	0.48	1.34	10.26
		<i>min</i>	34.54	8.08	7.71	1.54	0.41	0.11	0.77	0.08	0.51	1.00
1 to 2	pulv coal	<i>ave.</i>	51.76	26.85	10.32	1.47	0.97	0.24	2.62	0.25	1.46	0.90
		<i>s.d.</i>	2.32	2.46	1.80	0.47	0.15	0.12	0.29	0.09	0.15	0.43
		<i>count</i>	16	16	16	16	16	16	16	16	16	16
		<i>max</i>	55.85	32.62	13.26	2.60	1.39	0.56	3.30	0.41	1.69	1.78
		<i>min</i>	46.91	22.54	7.26	0.91	0.75	0.13	2.14	0.14	1.13	0.16

Table 3—Continued.

%S feed coal	type	sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	SO ₃	
1 to 2	reject	<i>ave.</i>	29.21	10.35	44.96	4.32	0.91	0.17	1.26	0.14	0.75	4.07	
		<i>s.d.</i>	12.91	5.73	22.14	5.13	1.46	0.26	0.74	0.10	0.33	4.86	
		<i>count</i>	17	17	17	17	17	17	17	17	17	17	17
		<i>max</i>	48.43	20.59	81.86	20.42	6.34	1.08	2.97	0.44	1.37	18.20	
		<i>min</i>	5.10	1.61	15.71	0.15	0.03	0.01	0.17	0.03	0.27	0.03	
2 to 3	pulv coal	<i>ave.</i>	45.58	21.30	18.72	2.61	0.99	0.37	2.58	0.37	1.16	2.54	
		<i>s.d.</i>	3.95	2.41	4.71	0.71	0.17	0.20	0.38	0.22	0.13	1.12	
		<i>count</i>	7	7	7	7	7	7	7	7	7	7	7
		<i>max</i>	52.93	25.42	27.44	3.50	1.20	0.71	3.05	0.64	1.31	3.86	
		<i>min</i>	41.69	17.77	13.03	1.88	0.71	0.20	2.06	0.18	1.02	1.45	
2 to 3	reject	<i>ave.</i>	17.07	4.73	64.26	3.41	0.50	0.22	0.57	0.27	0.38	5.18	
		<i>s.d.</i>	10.99	2.87	11.86	2.14	0.49	0.23	0.35	0.26	0.14	5.04	
		<i>count</i>	5	5	5	5	5	5	5	5	5	5	5
		<i>max</i>	35.65	9.65	75.79	6.23	1.36	0.52	1.18	0.73	0.61	13.71	
		<i>min</i>	8.32	2.24	47.78	0.48	0.14	0.04	0.27	0.10	0.23	0.61	
>3	pulv coal	<i>ave.</i>	45.79	19.42	20.16	3.61	0.89	0.39	2.50	0.26	1.00	3.74	
		<i>s.d.</i>	3.24	1.51	4.12	1.29	0.13	0.09	0.46	0.08	0.07	2.28	
		<i>count</i>	17	17	17	17	17	17	17	17	17	17	17
		<i>max</i>	50.49	21.89	28.68	7.49	1.09	0.55	3.24	0.37	1.14	11.21	
		<i>min</i>	40.27	15.57	14.69	2.10	0.63	0.22	1.68	0.10	0.91	1.91	
>3	reject	<i>ave.</i>	13.91	4.74	65.47	4.22	0.38	0.23	0.61	0.54	0.74	4.35	
		<i>s.d.</i>	9.79	3.54	14.63	2.03	0.21	0.17	0.45	0.64	1.25	2.56	
		<i>count</i>	17	17	17	17	17	17	17	17	17	17	17
		<i>max</i>	46.57	15.96	85.34	6.91	0.72	0.69	1.82	2.62	5.15	8.16	
		<i>min</i>	3.21	0.93	21.58	0.85	0.08	0.04	0.14	0.05	0.12	1.06	

Table 3c

%S	type	sample	Se (whole coal)	Hg (whole coal)	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Zr	Mo	Cd	Sb	Ba	Pb	
<1	pulv coal	<i>ave.</i>	5.86	0.07	281	105	193	29	123	235	157	53	13	1348	115	139	1	2	1227	52	
		<i>s.d.</i>	2.11	0.02	99	37	67	6	58	78	57	31	10	823	142	94	0	2	671	14	
		<i>count</i>	7	7	7	7	7	7	7	7	7	7	7	4	7	7	7	5	5	7	7
		<i>max</i>	7.94	0.09	392	148	270	37	216	358	251	122	28	2882	329	243	1	5	2721	67	
		<i>min</i>	1.51	0.05	147	57	119	24	37	154	80	36	6	636	1	24	1	1	792	33	
<1	reject	<i>ave.</i>	18.26	0.68	145	161	1099	57	58	79	196	185	107	557	129	110	7	7	572	69	
		<i>s.d.</i>	26.20	0.49	81	187	1111	28	28	80	378	131	134	374	64	42	12	4	422	27	
		<i>count</i>	9	10	9	10	10	10	8	9	8	10	2	9	10	4	10	10	10	10	
		<i>max</i>	87.00	1.60	278	688	3670	103	93	215	1128	505	201	1132	201	170	30	12	1679	124	
		<i>min</i>	6.05	0.24	6	54	213	21	13	10	23	66	12	57	29	74	1	1	215	27	
1 to 2	pulv coal	<i>ave.</i>	4.76	0.11	291	103	174	39	94	204	138	153	19	1115	218	79	4	4	1161	66	
		<i>s.d.</i>	1.14	0.03	86	42	79	5	34	54	48	96	17	445	131	68	4	3	256	18	
		<i>count</i>	9	16	16	16	16	16	16	16	16	16	3	16	15	16	10	8	16	16	
		<i>max</i>	6.24	0.19	442	187	410	47	155	341	260	403	38	2424	415	208	10	10	1635	103	
		<i>min</i>	2.75	0.03	186	60	109	29	40	131	74	52	8	493	47	17	1	1	728	36	
1 to 2	reject	<i>ave.</i>	25.50	1.59	152	103	484	107	39	162	409	683	25	248	142	40	26	14	405	155	
		<i>s.d.</i>	27.57	1.17	220	42	253	50	41	263	1167	687	13	203	80	6	31	7	223	120	
		<i>count</i>	11	17	14	17	17	17	11	11	11	17	3	13	17	2	17	17	17	17	
		<i>max</i>	71.00	3.85	878	168	1177	194	146	923	3922	2211	36	780	264	44	90	30	839	440	
		<i>min</i>	3.23	0.23	20	58	170	34	7	12	13	59	10	40	3	36	1	6	11	27	
2 to 3	pulv coal	<i>ave.</i>	3.27	0.14	368	164	316	53	108	117	251	144	23	675	195	61	1	6	841	57	
		<i>s.d.</i>	1.25	0.06	60	22	74	12	55	69	219	49	6	506	70	47	0	2	451	10	
		<i>count</i>	5	7	7	7	7	7	7	7	7	7	3	7	7	6	7	7	7	7	
		<i>max</i>	5.26	0.22	465	186	428	75	183	237	645	211	29	1247	277	144	1	10	1382	67	
		<i>min</i>	2.21	0.05	317	123	229	40	51	45	57	58	18	226	123	22	1	4	357	40	
2 to 3	reject	<i>ave.</i>	32.32	1.69	68	160	355	149	38	132	227	83	204	2	17	380	32				
		<i>s.d.</i>	39.25	0.76	55	40	43	29	24	129	104	98	0	3	204	21					
		<i>count</i>	6	5	5	5	5	5	4	2	5	1	5	4	5	5	5				
		<i>max</i>	89.00	2.30	162	210	387	183	69	223	310	83	263	2	21	591	54				
		<i>min</i>	2.90	0.41	31	112	301	122	12	40	60	83	32	2	13	95	4				

Table 3—Continued.

Table 3c			Se (whole coal)	Hg (whole coal)	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Zr	Mo	Cd	Sb	Ba	Pb	
%S	type	sample																			
>3	pulv coal	ave.	2.83	0.10	982	117	293	54	192	244	310	71	49	332	147	44	14	9	730	45	
		s.d.	2.50	0.05	1509	56	75	8	254	480	291	40	27	163	13	22	15	4	264	15	
		count	16	17	17	17	17	17	16	16	17	17	4	17	17	13	16	16	17	17	
		max	10.97	0.27	4871	259	473	66	769	1806	1144	176	78	646	167	83	40	20	1246	75	
		min	1.00	0.04	108	58	188	41	6	22	74	28	13	27	124	4	1	5	296	22	
>3	reject	ave.	29.50	1.47	56	121	411	151	36	25	145	217		86	136	6	39	24	416	75	
		s.d.	32.00	0.52	38	49	261	38	18	13	193	123		47	124	39	7	257	39		
		count	16	17	11	17	17	17	11	8	11	17		9	17	1	17	17	16	13	
		max	85.00	2.44	147	202	1313	209	64	55	658	451		182	271	6	90	30	1039	128	
		min	3.70	0.62	21	63	131	50	2	11	21	47		35	5	6	1	10	33	5	

coals, As, Se, and Hg are higher in the low- to middle-S range than in the highest S coals. This is, in part, a function of the chemical differences between source coals, with many of the 1–2% S coals coming from the eastern Kentucky counties to the northwest of the

Pine Mountain thrust fault, a region of know higher concentrations in trace elements (Sakulpitakphon et al., 2004).

3.2.1 Se distribution in feed coal and pulverized rejects

The correlation of pyritic S (wt. %) to Se for the pulverized feed coals and the pulverizer rejects from the 2002, 2004, and 2007 collections (Appendix Tables A1 and A2; with the addition of the data from Mardon and Hower [2004, their Table 2]) is shown on Figure 1a. Two distinct trends exist; one for the pulverized feed coals and another for the high-S pulverizer rejects. There is no apparent trend for the high-S pulverizer rejects, with clusters in both the high- and low-Se range at high S_{py} , but the (relatively) low-S feed coals have a negative correlation between Se and pyritic S (detail on Figure 1b). An anomalously high point (0.63% S_{py} and 11 $\mu\text{g/g}$ Se) is at a unit where all of the coal is pulverized, in contrast to the other units represented on Figure 1b. The anomalously low points (0.06% S_{py} with 1 $\mu\text{g/g}$ Se and 0.14% S_{py} with 1.29 $\mu\text{g/g}$ Se) are from a unit burning a Cretaceous western US bituminous: Paleocene Powder River Basin subbituminous coal blend. The other units are all burning Pennsylvanian eastern US (both Appalachian and Illinois basins) bituminous coals.

Not considering the outliers explainable by other factors, why is there a negative correlation between S_{py} and Se? Significant amounts of the Se in coal are associated with selenides, not sulfides (Hower and Robertson, 2003), and some Se is organically bound (Yudovich and Ketris, 2006; Riley et al., 2007). Within pyrite and marcasite, Hower et al. (2008a) found an 11–250 $\mu\text{g/g}$ range in Se concentration. The form of Se in coal has only minor impact on its volatilization in combustion (Senior et al., 2001).

With Se concentrations of only a few $\mu\text{g/g}$, slight deviations in the amount of different Se forms would significantly alter the correlation between Se and a major element (S) with which it has only partial association. In addition, the higher- S_{py} coals are from the Illinois Basin and the latter coals tend to have lower amounts of accessory elements in sulfides than do Appalachian coals (Palmer and Lyons, 1990; Hower et al., 2005b).

3.3 Element distribution in fly ash

The summary of the chemistry of the first and second row ESP's, as grouped by S content of the feed coal, is presented in Table 4. Only the first two ESP rows are included in the table because of the relative lack of data from later ESP rows.

There is an overall increase in Fe_2O_3 , CaO, and SO_3 , and an accompanying decrease in SiO_2 and Al_2O_3 , in the fly ashes from the

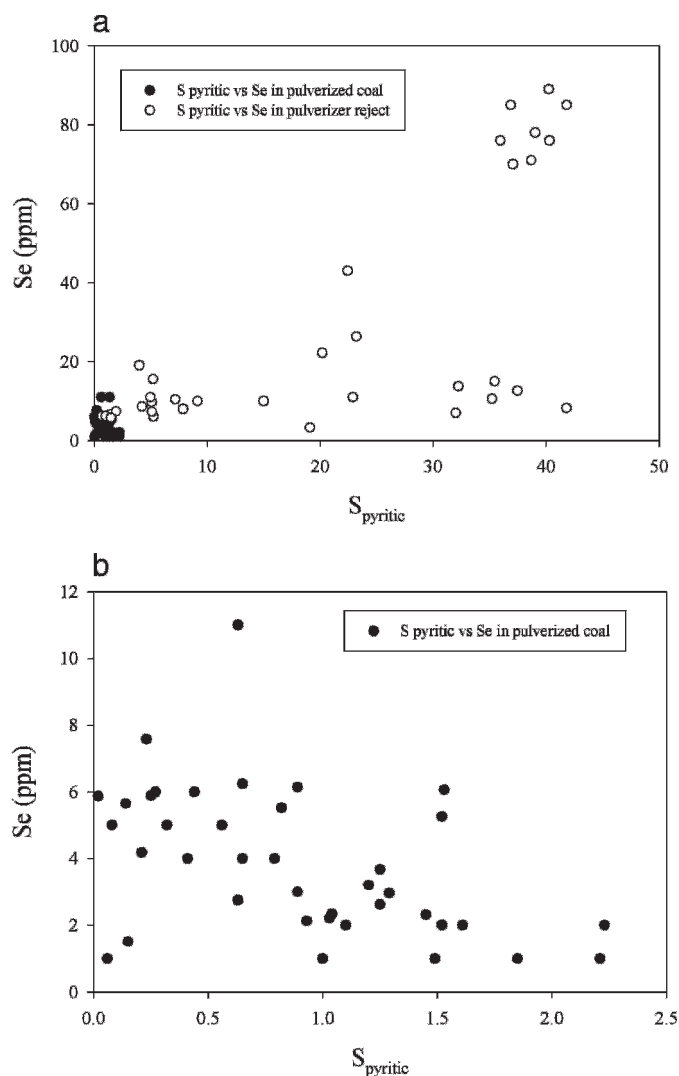


Fig. 1a. Selenium ($\mu\text{g/g}$) versus pyritic sulfur (%) in pulverized coals and pulverizer rejects from Kentucky power plants for 2002, 2004, and 2007 samplings.

Fig. 1b. Selenium ($\mu\text{g/g}$) versus pyritic sulfur (%) in pulverized coals and pulverizer rejects for the 0–12 $\mu\text{g/g}$ Se and 0–2.5% pyritic S range from the same collection as in Figure 1a.

Table 4

a/ Summary of ultimate analysis (%_{as-received} basis) for first and second row ESP fly ashes from 2007 sampling of Kentucky power plants. b/ Summary of major oxides (%_{ash} basis) for first and second row ESP fly ashes from 2007 sampling of Kentucky power plants. c/ Summary of minor elements (ppm on ash basis) for first and second row ESP fly ashes from 2007 sampling of Kentucky power plants.

%S in feed coal	row		Ash	Moisture	C	H	N	S	O
<1	1	av	92.72	0.28	6.12	0.06	0.06	0.22	0.86
		st dev	5.34	0.25	4.82	0.05	0.04	0.12	0.64
		number	22	22	22	19	13	22	22
		max	98.81	0.85	14.37	0.20	0.12	0.46	3.18
		min	81.69	0.05	0.74	0.01	0.02	0.09	0.28
<1	2	av	92.09	1.00	5.88	0.15	0.07	0.26	1.61
		st dev	5.33	2.20	4.89	0.29	0.05	0.10	2.04
		number	19	19	19	16	9	19	19
		max	99.52	7.37	16.26	0.91	0.15	0.47	7.29
		min	82.10	0.04	0.28	0.01	0.01	0.07	0.12
1 to 2	1	av	93.40	0.19	5.89	0.04	0.04	0.18	0.54
		st dev	3.56	0.11	3.26	0.03	0.04	0.07	0.23
		number	10	10	10	10	7	10	9
		max	96.82	0.41	14.25	0.10	0.12	0.32	0.91
		min	84.36	0.10	2.95	0.01	0.01	0.11	0.27
1 to 2	2	av	89.19	0.31	9.60	0.08	0.08	0.29	0.77
		st dev	5.97	0.23	5.47	0.05	0.09	0.09	0.47
		number	10	10	10	10	9	10	10
		max	94.99	0.92	24.12	0.21	0.30	0.45	1.86
		min	73.13	0.17	4.14	0.04	0.01	0.17	0.26
2 to 3	1	av	92.72	0.51	5.78	0.10	0.04	0.54	1.01
		st dev	6.33	0.51	5.70	0.08	0.03	0.13	0.61
		number	14	14	14	13	7	14	12
		max	99.27	2.02	19.75	0.29	0.09	0.85	2.48
		min	78.07	0.04	0.42	0.02	0.01	0.34	0.12
2 to 3	2	av	90.45	0.57	7.95	0.12	0.09	0.63	1.18
		st dev	8.05	0.42	7.37	0.05	0.09	0.16	0.66
		number	14	14	14	13	8	14	10
		max	99.20	1.69	25.03	0.22	0.31	1.06	2.35
		min	71.97	0.05	0.44	0.04	0.01	0.43	0.30
>3	1	av	91.75	0.37	6.79	0.09	0.17	0.78	0.71
		st dev	11.08	0.37	10.12	0.10	0.04	0.81	1.15
		number	17	17	17	15	3	17	16
		max	98.79	3.82	74.80	4.93	1.44	4.85	11.45
		min	6.52	0.09	0.76	0.02	0.13	0.21	0.01
>3	2	av	88.22	0.47	9.39	0.13	0.12	1.17	1.47
		st dev	10.82	0.26	10.35	0.11	0.06	0.92	1.39
		number	11.00	11.00	11.00	11.00	4.00	11.00	9.00
		max	98.59	1.09	29.89	0.37	0.16	2.94	4.94
		min	68.47	0.21	0.66	0.03	0.03	0.36	0.35

Table 4b

%S in feed coal	row		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	SO ₃
<1	1	av	54.78	29.49	5.86	2.14	1.12	0.55	2.64	0.23	1.50	0.24
		st dev	2.61	1.55	0.69	1.78	0.49	0.68	0.55	0.19	0.14	0.22
		number	22	22	22	22	22	22	22	22	22	22
		max	57.79	31.46	7.46	7.66	2.65	2.54	3.10	0.70	1.73	0.90
		min	47.30	25.87	4.95	1.09	0.80	0.20	1.00	0.09	1.10	0.06
<1	2	av	54.21	29.62	5.98	2.32	1.19	0.61	2.72	0.24	1.51	0.31
		st dev	1.84	1.52	1.05	1.78	0.49	0.70	0.62	0.18	0.16	0.24
		number	19	19	19	19	19	19	19	19	19	19
		max	56.26	32.00	9.06	7.51	2.60	2.46	3.21	0.70	1.71	0.99
		min	49.58	26.01	5.05	0.98	0.82	0.20	1.01	0.10	1.09	0.06
1 to 2	1	av	53.03	28.53	11.47	1.29	0.90	0.17	2.56	0.26	1.43	0.16
		st dev	1.48	1.63	2.45	0.26	0.17	0.03	0.35	0.14	0.09	0.26
		number	10	10	10	10	10	10	10	10	10	10
		max	55.51	31.63	16.67	1.89	1.14	0.23	3.07	0.58	1.59	0.87
		min	50.76	25.54	7.60	0.99	0.69	0.13	2.14	0.15	1.31	0.02

Table 4.—Continued.

%S in feed coal	row		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	SO ₃	
1 to 2	2	av	51.97	28.93	11.49	1.43	0.95	0.19	2.67	0.32	1.46	0.11	
		st dev	0.70	1.25	2.02	0.25	0.16	0.03	0.29	0.14	0.07	0.09	
		number	10	10	10	10	10	10	10	10	10	10	10
		max	53.03	31.81	13.30	2.04	1.17	0.23	3.09	0.65	1.58	0.36	
		min	50.82	27.74	6.67	1.26	0.77	0.15	2.31	0.20	1.33	0.05	
2 to 3	1	av	47.29	19.50	21.78	4.48	0.88	0.62	2.36	0.19	1.03	1.75	
		st dev	7.56	4.17	10.22	1.26	0.17	0.29	0.55	0.09	0.19	1.77	
		number	14	14	14	14	14	14	14	14	14	14	
		max	52.54	22.85	55.23	6.01	1.08	1.25	2.87	0.37	1.14	7.75	
		min	22.18	5.91	16.96	2.86	0.38	0.28	0.66	0.10	0.42	0.73	
2 to 3	2	av	48.45	20.59	19.24	4.43	0.93	0.66	2.55	0.21	1.10	1.40	
		st dev	2.31	1.54	3.85	1.37	0.11	0.27	0.31	0.07	0.05	0.37	
		number	14	14	14	14	14	14	14	14	14	14	
		max	51.70	23.62	28.95	6.37	1.12	1.13	3.08	0.34	1.18	1.85	
		min	42.95	18.17	15.95	2.71	0.73	0.31	2.08	0.12	1.01	0.77	
>3	1	av	47.03	20.09	19.48	5.59	0.95	0.40	2.73	0.26	1.00	2.61	
		st dev	3.28	2.05	2.48	2.64	0.12	0.14	0.45	0.06	0.13	3.90	
		number	17	17	17	17	17	17	17	17	17	17	
		max	49.91	22.73	31.19	13.51	1.13	0.87	3.25	0.36	1.15	12.88	
		min	34.48	13.37	16.60	1.31	0.63	0.26	1.42	0.09	0.68	0.31	
>3	2	av	45.44	19.75	19.56	6.11	0.99	0.45	2.81	0.26	1.01	3.63	
		st dev	4.18	2.45	3.38	3.77	0.11	0.23	0.44	0.05	0.15	4.95	
		number	11	11	11	11	11	11	11	11	11	11	
		max	50.06	22.59	28.63	15.15	1.16	1.09	3.37	0.31	1.25	14.28	
		min	38.48	15.55	14.93	3.36	0.85	0.30	1.98	0.14	0.67	0.77	

Table 4c

%S in feed coal	row		Se	Hg	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Zr	Mo	Cd	Sb	Ba	Pb	
<1	1	av	12.78	0.26	385	131	204	27	127	270	198	49	22	1484	37	156	1	2	1226	65	
		st dev	15.86	0.44	66	24	64	5	33	73	49	27	11	1079	14	57	0	1	878	13	
		number	21	22	22	22	22	22	22	22	22	22	22	15	22	17	22	22	11	22	22
		max	61.38	1.44	501	162	371	35	196	434	330	138	40	4532	58	247	1	2	3880	106	
		min	0.25	0.01	212	67	109	14	48	146	121	22	3	638	5	79	1	1	680	50	
<1	2	av	14.25	0.23	410	138	220	29	144	297	259	64	31	1463	37	161	1	2	1680	71	
		st dev	17.33	0.35	78	29	57	6	41	79	104	27	19	1136	15	67	0	1	1733	14	
		number	19	19	19	19	19	19	19	19	19	19	7	19	15	19	19	8	19	19	
		max	66.24	1.14	495	183	312	40	205	407	571	115	70	4418	63	268	1	3	7886	96	
		min	0.29	0.01	200	73	124	14	46	135	98	26	13	372	20	76	1	1	744	49	
1 to 2	1	av	17.94	0.33	370	140	164	40	110	219	138	117	16	1199	63	135	1	3	1017	76	
		st dev	6.84	0.22	51	16	26	7	20	58	56	91	13	300	18	56	0	1	87	42	
		number	10	10	10	10	10	10	10	10	10	10	2	10	9	10	10	10	10	10	
		max	30.24	0.72	491	183	201	54	158	337	285	361	25	1913	102	242	1	5	1155	191	
		min	6.99	0.12	313	128	119	29	87	105	68	49	6	772	38	50	1	1	888	51	
1 to 2	2	av	30.12	0.76	409	152	172	43	129	262	184	177	24	1247	56	146	1	3	1141	101	
		st dev	10.42	0.32	42	18	29	7	18	57	60	115	8	281	21	48	0	1	99	52	
		number	10	10	10	10	10	10	10	10	10	10	2	10	10	10	10	10	10	10	
		max	45.96	1.17	519	199	220	48	170	357	322	469	29	1969	75	243	1	4	1288	235	
		min	11.06	0.22	368	138	148	25	106	181	123	52	18	1017	5	106	1	2	954	59	
2 to 3	1	av	12.78	0.18	388	158	281	51	85	34	251	71	12	221	134	43	1	6	591	39	
		st dev	10.34	0.22	125	34	48	3	10	14	111	18	8	174	12	26	0	1	197	13	
		number	12	14	14	12	12	12	12	12	4	12	12	7	12	12	11	12	12	12	12
		max	31.00	0.80	599	227	347	55	111	46	451	103	24	608	159	96	1	8	1019	70	
		min	0.58	0.01	121	124	207	46	73	15	158	54	3	71	123	21	1	5	431	27	
2 to 3	2	av	15.89	0.27	441	169	291	50	96	35	312	82	14	243	132	53	1	6	621	41	
		st dev	9.17	0.27	135	42	55	2	21	21	124	18	8	202	11	32	0	1	192	9	
		number	12	14	14	12	12	12	12	12	6	12	12	3	12	12	12	12	12	12	
		max	29.00	0.83	787	252	359	53	152	64	524	125	23	737	148	127	1	8	1024	65	
		min	0.08	0.01	302	128	208	46	76	13	193	63	8	57	108	23	1	4	443	33	
>3	1	av	25.89	0.12	938	170	279	54	212	44	297	78	22	261	148	32	1	7	736	32	
		st dev	15.46	0.13	1421	40	61	7	301	39	290	34	12	253	17	21	0	2	262	10	
		number	15	17	17	17	17	17	17	17	13	17	17	8	16	17	16	17	17	17	
		max	47.00	0.50	7711	411	535	77	1353	135	1370	183	41	901	214	77	1	16	1611	56	
		min	0.83	0.01	120	92	185	42	26	1	53	40	1	17	109	3	1	5	258	6	

Table 4.—Continued.

Table 4c			Se	Hg	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Zr	Mo	Cd	Sb	Ba	Pb
>3	2	av	21.94	0.38	1294	183	291	55	305	85	589	114	16	181	153	40	1	7	686	44
		st dev	13.11	0.51	1705	47	76	11	361	62	974	68	8	76	13	23	0	2	295	18
		number	11	11	11	11	11	11	11	8	11	11	3	10	11	11	11	11	11	11
		max	47.00	1.67	4681	279	417	82	994	224	3520	301	25	304	181	71	1	12	994	85
		min	4.00	0.02	243	105	176	37	65	24	191	50	11	46	138	3	1	5	240	21

higher-S coals. Volatile trace elements, such as Zn and As, increase from the first to second ESP rows, as expected. Arsenic, Hg, and Pb reach their highest concentrations in the fly ashes from the 1–2%S coals. The increase in Hg from the first to second ESP rows is a function of both the T decrease and the C increase in the same direction.

3.3.1 Selenium distribution in Kentucky fly ashes

A number of trends are seen among the Kentucky power plants sampled in 2002 (Appendix Table A2). For example, plant T, burning a blend of high volatile C bituminous, high-S western Kentucky coals, shows an increase in Se from 5 to 80 $\mu\text{g/g}$ across four ESP rows in the direction of cooler flue gas temperatures. In contrast, plant G, burning a western US high volatile C bituminous: Powder River Basin subbituminous coal blend, has a peak Se of 74 $\mu\text{g/g}$ in the third row of the comparatively warm ($>170^\circ\text{C}$) mechanical separation system (this is the coolest row of the mechanical part of the ash-collection system, but still somewhat warmer than the baghouse system). The first row of the plant G mechanical fly ash separation system has 2 $\mu\text{g/g}$ Se, decreasing to 11–15 $\mu\text{g/g}$ Se in the baghouse ash. Plants A and E, with multiple units at each plant, had hot-side ESP collection systems, mitigating against the capture of Se and other volatile trace elements.

The plants selected for further study in the 2004 sampling included two plants (H and I), both with feed coal from eastern Kentucky sources, known to have relatively high Se, As, and Hg concentrations in their fly ash (Appendix Table A2). Particularly for plant I, both Hg and As increase in concentration towards the cooler end of the ESP array, with Hg showing the anticipated relationship with fly ash C and flue gas temperature (Figure 2; with data in Appendix A2 [plant I for 2004]). For the 2004 sampling, plant I Hg increases from 0.27 $\mu\text{g/g}$ in the first ESP row to 1.84 $\mu\text{g/g}$ in the third row. This is expected, both on the basis of the temperature decrease in the same direction and the increase in average fly ash C from 5.39% to 19.28%. Arsenic increases from

133 to 314 $\mu\text{g/g}$ from the first to the third row, while Se increases from 5.5 to 12 $\mu\text{g/g}$. The pattern for Se is less obvious; none of the 2002 or 2004 samplings exhibited the extreme concentration in the first row ESP noted by Mardon and Hower (2004). In fact, plant I, the site of their study, shows an increase, albeit subtle, in Se with a decrease in temperature in the 2004 samples, closer to the expected behavior for such a volatile element. The 2002 sampling at the latter plant did not have enough samples to clearly define a trend. For the 2004 sampling, plant H Hg increases from 0.12 $\mu\text{g/g}$ in the first ESP row to 0.92 $\mu\text{g/g}$ in the fourth ESP row (there is a fifth row, but no ash could be sampled). Arsenic increases from 62 to 206 $\mu\text{g/g}$ in the same direction. Selenium, however, increases from 4 $\mu\text{g/g}$ in the first row to 11.3 $\mu\text{g/g}$ in the third row, but then decreases to 5.2 $\mu\text{g/g}$ in the fourth row. The plant E cool-side ESP has higher Se in the first row of both the A and B sides, but the difference is slight, probably within the error of the analysis. Selenium passes through a minimum in the second of the three ESP rows. Arsenic increases slightly from the first to third ESP rows. Hg increases from the first to third rows on side A, but peaks in the first row on side B, following the peak in C concentration. The hot-side ESP has negligible Se, generally below the detection limit, and has very low Hg concentrations.

Based on previous studies, it is not a surprise that, among the Kentucky plants, plant I has the higher Hg and As values. The Se distribution, however, remains problematical. There is no consistent pattern related to the ESP row, therefore flue gas temperature or fly ash particle size (decreasing from the first to the third ESP rows), in Se distribution. The extraordinarily high first row values, average of 155 $\mu\text{g/g}$, noted by Mardon and Hower (2004) from their 2001 sampling of plant I, or the 37 $\mu\text{g/g}$ Se values for the first and second rows in the 2002 sampling of the same plant, are not observed here. It is certainly possible that the reconfiguration of the ash collection system, the mechanical separation in place in 2001 and 2002 was bypassed by 2004, with the entire volume of fly ash passing to the ESP array, changed the bulk chemistry of the ash. The distribution of Se not only does not appear to be consistent from sampling to sampling, even accounting for differences in concentration in the feed coals, but it does not appear to follow the patterns known for other volatile elements.

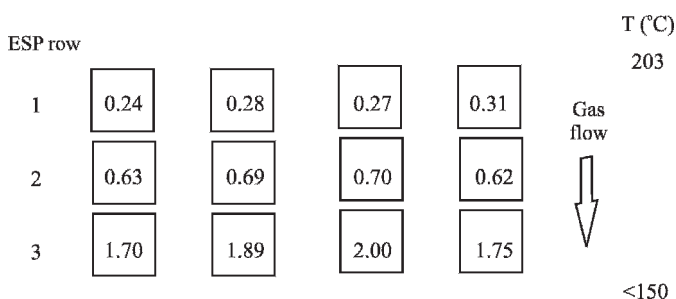


Fig. 2. Distribution of Hg versus ESP hoppers for plant I (2004 sampling).

4. Summary

1. The total production of coal combustion products from Kentucky utilities in 2006 exceeded 8 Mt. The rate of utilization increased to 30%, up from 10% in 1996 and 20% in 2001. Much of the increase can be attributed to an increase in both FGD gypsum production and utilization percent, although both fly ash and bottom ash/slag contributed to the increased utilization.

2. The concentration of trace elements in the feed coal and in the pulverizer reject is somewhat independent of the sulfur content of the feed coal. Many of the volatile trace elements can have an association with pyritic sulfur. Provincial variations in trace element contents influence the averages, with some of the intermediate-S coals coming from the portion of eastern Kentucky with elevated trace element contents in the sulfides.
3. In the first and second row ESP fly ashes, there is a general increase in Fe₂O₃, CaO, and SO₃, and an accompanying decrease in SiO₂ and Al₂O₃, with an increase in the S content of the feed coal. Arsenic, Pb, and Hg attain their highest concentration in the ashes from the 1–2%S feed coals. Within each feed-coal-S group, there is an increase in the concentration of most volatile trace elements from the first to second ESP rows, a function of the decreasing flue gas temperature and of the decreasing fly ash particle size towards the back ESP rows. Mercury is an exception, being dependant on the concentration of carbon in the fly ash in addition to the flue gas temperature.
4. Selenium shows no consistent pattern of concentration with the ESP row. In some cases, there is an increase in concentration towards the cooler ESP rows. In one case, the relatively high Se concentrations in the first ESP row observed in samples collected in 2001 and 2002 were not observed in the 2007 samples. In the latter case, the reconfiguration of the ash-collection system might have played a role in the trace element distribution.

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APPENDIX A1.

Proximate and ultimate analyses (% as-received basis); forms of sulfur (% as-received basis); heating value (Megajoules/kg, as-received basis); Chlorine (ppm ($\mu\text{g/g}$), as-received basis); major oxides (% ash basis); and minor elements (ppm ($\mu\text{g/g}$) on ash basis for all except Hg on whole-coal basis) for pulverized coals and pulverizer rejects from 2002, 2004, and 2007 samplings of Kentucky power plants.

APPENDIX A2.

Ultimate analyses (% as-received basis); major oxides (% ash basis); and minor elements (ppm ($\mu\text{g/g}$) on ash basis for all except Hg on whole-coal basis) for first and second row ESP fly ashes from 2002, 2004, and 2007 samplings of Kentucky power plants.