"Arsenic and Silicon Behavior in Combustion and Gasification: Some Practical Implications"

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Motivation

- Submicron Ash Formed by Vaporization and Condensation during Coal Combustion and Gasification of Concern as a Consequence of:
 - Blinding of Filters
 - Deposition on Heat Transfer Surfaces (Glue for larger particles)
 - Health impacts
 - Nanoparticles
 - Trojan horses for toxic compounds
- Arsenic is a trace compound of concern for health impacts
 - Health impacts during tube cleaning
 - Reduction in efficiency of SCR catalysts
 - Leaching from ash ponds into water supply

Message

 Fundamental understanding, although incomplete, provides basis for development of models to address real world problems

Vaporization of Refractory Oxides

- Principal source of mass of submicron particles
- Augmented by reduction to oxides to more volatile suboxides and metals
- Can be modeled given T, O₂ history
- Models can incorporated into CFD codes to predict effect of combustion conditions
- Fate of Trace Quantities of Arsenic in Coal
 - Upon combustion, a portion of the arsenic in coal vaporizes.
 - The vaporized arsenic partitions to fly ash in the postcombustion flue gas by heterogeneous condensation and surface reaction with calcium in the ash.
 - Calcium is sulfated by reaction with SO₂, thus decreasing ash surface reactivity with arsenic.
 - Can be modeled given coal composition and profiles of, combustion stoichiometry, temperature of flue gases, ash size and calcium distributions.
 - Fractional arsenic vaporization (provides initial gas and ash arsenic concentrations).
 - Results include vapor-phase arsenic, and arsenic in ash profiles



Bi-Modal Size Distribution



Laboratory Data of Neville et al. (1981) 5

Oxygen mainly influences submicron fraction

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Quann Vaporization Model





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Modeling of CO/CO₂ Ratio



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Predicted Concentration Profiles $d=100\mu m$, $O_2 = 10\%$, Ta = 1700 K, $T_s=1980$ using SKIPPY (Haynes)



Front Wall – 500 MW_e PC-Fired Utility Boiler w/Advanced OFA, Davis et al.



Boiler Simulation



 Used furnace symmetry modeled half of boiler

Over
500,000
computation
al cells.

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Ash Vaporization Can Be Followed Along Each Particle Path -e.g., Rear Bottom Burner



Particles Exiting Inner Annulus 77 West 200 South, Suite 210, Salt Lake City, Utah 84101, TEL (801) 364-6925



Particles Exiting Outer Elipses Reaction Engineering International



Reducing Burner Mixing Intensity can³ Reduce Vaporization (Chudnovsky, 2001)



Particles diameter - micron

Transition to Arsenic

- Refractory oxide vaporization can be estimated for different streamlines
- Question now is how arsenic in ash is distributed between vapor and ash, allowing for:
 - -Vaporization in the radiant section
 - -Reaction with Ca along trajectories
 - Neutralization of Ca by reaction with SO₂

% As in residual char or ash vs pyrolyis T or %O₂



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Coal Composition

	Illinois	Pittsburgh	Ohio	Kentucky	Wyodac	North
	Bit.	Bit.	Bit.	Bit.	Sub-Bit.	Dakota
						Lignite
С	67.69%	76.62%	69.16%	74.87%	37.13%	23.30%
Н	4.73%	4.80%	4.93%	4.59%	4.72%	3.98%
Ν	1.18%	6.91%	1.33%	1.43%	0.52%	0.25%
S	3.60%	1.48%	2.55%	0.82%	0.23%	0.38%
CI (ppmw)	340	16400	948	1700	18.9	21.7
0	9.20%	0.10%	9.90%	8.38%	25.55%	26.83%
Ash	10.26%	7.01%	9.70%	7.41%	6.03%	9.38%
Moisture	3.31%	1.44%	2.33%	2.33%	25.81%	35.88%
Arsenic in coal (ppmw, AR)	2.7	4.1	17.39	4	1.38	7.36
CaO in Ash (g/g ash)	4.19%	4.58%	2.24%	1.95%	22.74%	30.25%
Ca/S (g/g, coal)	0.0031	0.0023	0.0016	0.0010	0.0098	0.0203
Ca/As (g/g, coal)	1138.303927	558.88961	89.24669	257.3694	7097.42236	2753.736413
Combustion SR	1.2	1.2	1.2	1.2	1.2	1.2

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Arsenic Vaporization, Literature



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Model Equations

• The following equation tracks the concentration of arsenic in the ash particles as a function of time:

$$C_{As,i} = C_{Aso,i} + \frac{4 \cdot MW_{As}}{\frac{\pi}{6} \cdot \rho_i \cdot d_i^3} \cdot \int_{t=0}^{t=tf} F_i(t) \cdot dt$$

- The first term on the right is the initial concentration due to arsenic not vaporized on combustion.
- The integral term is the flux of vapor to the surface by condensation or surface reaction. The flux depends on the concentration of arsenic in the vapor, the active ash surface area for reaction with calcium, and the gas temperature.
- Four flux equations are used : reaction and condensation fluxes for sub- and super-micron particles, accounting for free molecular, and continuum fluid regimes, respectively.

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Arsenic Flux Equations

	Sub-Micron	Super-Micron
Arsenic Heterogeneous Condensation	$F_{i} = \frac{\psi \cdot \pi \cdot d^{2} \cdot (P_{As,b} - P_{As,s})}{\left(2 \cdot \pi \cdot MW \cdot R \cdot T\right)^{1/2}}$	$F_{i} = \frac{2\pi \cdot d_{i} \cdot D}{R \cdot T} \cdot \left(P_{As,b} - P_{As,s}\right) \cdot \left[\frac{1 + Kn}{1 + 1.71 \cdot Kn + 1.33 \cdot Kn^{2}}\right],$ term = (cfs)
Arsenic Surface Reaction	$F_i = \frac{\pi d^2}{R \cdot T} \cdot k_s \cdot P_{As,b} \cdot Fasa$	$F_{i} = \pi \cdot d_{i}^{2} \cdot \frac{P_{As,b}}{R \cdot T} \left[\frac{1}{\frac{1}{k_{s} \cdot Fasa} + \frac{d_{i}}{2 \cdot D \cdot cfs}} \right]$
SO ₂ Surface Reaction	$F_i = \pi \cdot d^2 \cdot k_s \cdot P_{SO2} \cdot Fasa$	$F_{i} = \pi \cdot d_{i}^{2} \cdot \frac{P_{SO2}}{R \cdot T} \left[\frac{1}{\frac{1}{k_{s} \cdot R \cdot T \cdot Fasa} + \frac{d_{i}}{2 \cdot D \cdot cfs}} \right]$

- F is the flux in moles As_4O_6 per second per particle.
- d is particle diameter, D is diffusivity, cfs is the Fuchs-Sutugin correlation for noncontinuum behavior.
- Kn is the knudsen number, and ψ is the accomodation coefficient, taken as 1.
- Fasa is the fraction of active surface area, taken as the percent CaO in a given ash particle size, and k_s is the intrinsic surface reaction rate constant.

Measured Size Distributions



Size (micron)

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Calcium Concentrations



Measurements are taken just after the flame, at around 1400 K. Experimental values have been normalized to agree with CaO in coal.

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Temperature Profile

Typical Boiler Gas Temperature Profile



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Arsenic-in-Ash Concentration (Illinois)



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Arsenic in Ash (North Dakota)



Pittsburgh Coal. Effect of Sulfur Concentration



Wyodak Profiles

Vapor-Phase As4O6 Concentration Profile



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Arsenic as As ₄ O ₆ , at 700 °F								
Coal	Initial Gas ppbv	Final Gas ppbv	Sulfur in Coal	CaO in Ash*	CaO/S (in coal)			
			wt%	wt%	g/g			
Illinois	17	12	3.6%	4.2%	0.12			
Pittsburgh	23	15	1.6%	4.6%	0.20			
Ohio	107	96	2.5%	2.2%	0.09			
Kentucky	23	22	0.8%	1.9%	0.18			
Wyodak	15	0	0.2%	22.7%	5.91			
North Dakota	115	1	0.4%	30.3%	7.46			

*SO₃-free basis

Conclusions

- Arsenic vaporization is higher for higher coal ranks, but this effect is primarily a function of flame temperature.
- The arsenic model correctly reproduced trends in pilot-scale data.
- Ca/S and Ca/As ratios affect the arsenic distribution:
 - Higher sulfur concentrations result in higher vapor arsenic concentrations, and lower arsenic recovery in ash, as expected, due to lower CaO availability in high sulfur coals.

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Ash Size Distributions

	Sub-micron	Weight %	Sub-micron	Surface	
	Weight	< 0.1 micron	Surface	Area	
	Percent		Area	Percent	
			Percent	< 0.1 micron	
Illinois 6 Bituminous	20.3%	2.04%	84.0%	50.87%	
Pittsburgh Bituminous	20.2%	3.32%	85.1%	55.07%	
Ohio Bituminous	10.3%	1.75%	62.2%	45.87%	
Kentucky Bituminous	10.0%	0.51%	54.1%	25.76%	
Wyodac Sub-Bituminous	30.7%	5.64%	88.5%	54.60%	
North Dakota Lignite	12.2%	2.77%	78.7%	53.04%	

	Weight Percent								
Size	Illinois 6	Pittsburgh	Ohio	Kentucky	Wyodac	North			
micron	Bituminous	Bituminous	Bituminous	Bituminous	Sub-	Dakota			
					Bituminous	Lignite			
0.0324	0.95%	0.76%	0.30%	0.23%	1.10%	0.57%			
0.0636	0.53%	1.54%	0.90%	0.16%	1.21%	0.90%			
0.0926	0.56%	1.02%	0.55%	0.13%	3.34%	1.31%			
0.168	0.69%	1.17%	0.28%	0.15%	3.89%	1.38%			
0.337	1.09%	2.01%	0.08%	0.40%	2.47%	1.78%			
0.535	4.99%	5.90%	0.18%	0.76%	6.64%	2.79%			
0.973	11.45%	7.83%	7.98%	8.20%	12.02%	3.45%			
1.96	6.07%	10.34%	28.52%	14.39%	21.07%	10.79%			
3.77	12.76%	12.55%	16.50%	21.15%	16.16%	22.60%			
7.33	46.25%	50.27%	32.64%	39.33%	22.58%	47.12%			
15.7	14.66%	6.61%	12.07%	15.12%	9.53%	7.33%			

Sizes < 0.1 micron assumed to constitute the submicron fume.

This is shown in the size distribution plots by the bimodal shape at 0.1-0.2 micron.

The literature reports that fume constitutes 1-3 wt% of the ash.

Measurements are taken at the furnace exit at around 1100 K.

Arsenic Vaporization

- Experimental arsenic in ash did not satisfy a material balance based on the coal composition. Experimental ash concentrations were normalized assuming 100% recovery of vaporized arsenic to ash.
- The degree of arsenic vaporization was estimated from the normalized experimental arsenic concentration on the larges ash sizes, which have the smallest vapor-phase arsenic flux.
- The literature indicates that arsenic not contained in silicates is expected to vaporize (> 85%).
- Arsenic vaporization is higher for higher coal ranks, but this effect is primarily a function of flame temperature.
- The initial arsenic concentration of particles < 0.1 μ is zero, since this ash is assumed to originate from condensation of vaporized ash.

Results	Measured	Illinois	Pittsburgh	Ohio	Kentucky	Wyodac	North
	Forms of Occurance						Dakota
	Organic	0.0%	0.0%	0.0%	0.0%	5.0%	0.0%
	Mono-sulfides	20.0%	10.0%	30.0%	30.0%	25.0%	60.0%
	Pyrite/sulfides	60.0%	80.0%	35.0%	35.0%	25.0%	15.0%
	Silicates	0.0%	0.0%	5.0%	5.0%	15.0%	10.0%
	Estimated As Vaporization						
	Based on As in Ash Conc.	72.6%	94.8%	77.7%	62.9%	56.3%	36.3%

Model Results

	Illinois	Pittsburgh	Ohio	Kentucky	Wyodak	North Dakota
	Bit.	Bit.	Bit.	Bit.	Sub Bit.	Lignite
Residence Time (s)	3.5	2.9	3.2	2.9	6.6	9.44
PeakTemperature (K)	1565	1565	1630	1660	1470	1425
Final Temperature (K)	1065	1065	1070	1220	960	868.541
Estimated Vaporization	72.6%	94.8%	77.7%	62.9%	56.3%	36.3%
% Recovery Vapor to Ash	37.8%	37.2%	14.1%	5.7%	100.0%	100.0%
Initial Vapor As ₄ O ₆ ppbv	16.3	29.2	111.1	19.6	11.0	55.8
Final Vapor As ₄ O ₆ ppbv	10.2	18.4	95.0	18.5	0.0	0.0
Exp.% As < 1 μm	44.3%	94.3%	59.8%	24.4%	54.1%	26.1%
Exp % As < 0.1 μm	0.9%	1.3%	2.6%	2.3%	16.2%	7.3%
Model %As < 1 µm	47.6%	83.6%	20.7%	12.5%	60.6%	32.4%
Model %As < 0.1 μm	9.5%	23.3%	1.9%	2.1%	38.6%	17.3%

Combustion S.R. = 1.2,

Assumed Experimental Recovery of Arsenic Vapor to Ash = 100%

- The above table lists the experimental residence time, peak and final temperatures, and the estimated arsenic vaporization used in the model.
- Kinetics for arsenic reaction with calcium oxide were taken from the literature. The preexponetial, k, was increased to match the experimental data (itself adjusted).

Model Tests

- Test the arsenic partitioning model for the six coals listed in the report "Toxic Substances from Coal Combustion-A Comprehensive Assessment", or "Toxics".
 - Coals cover a range of rank: Bituminous to Lignite
 - Range of calcium/sulfur ratios, and arsenic/calcium ratios.
 - Detailed coal properties, and operating conditions.
 - Data taken in a down-fired pilot scale furnace.
- Compare the model to experimental data.
- Results.
 - Vapor-phase arsenic at air preheater inlet.
 - Arsenic in ash concentration profiles.

Results

- Experimenal data for arsenic concentrations on fly ash did not satisfy a material balance, so the data were normalized assuming 100% recovery of vaporized arsenic. Thus, only the shape of the experimenal versus modeled distribution curves can be compared, not the absolute magnitudes.
- Submicron ash sizes are enriched in arsenic, due to the high surface area fraction of these particles.
- Since the initial arsenic concentration is zero for particles < 0.1 μ m, these particles can be depleted in arsenic relative to larger sizes.
- The model correctly predicts trends in the experimental data.
- The experimental CaO distributions for Illinois and Pittsburgh coals are suspect, since only two minerals in ash were reported for these coals.
- Coals with low vapor recovery to ash (Ohio and Kentucky) show much lower concentrations than the experimental data, assuming 100% arsenic recovery on ash.
- Coals with high Ca/As ratios and low sulfur (Wyodak, and North Dakota), show significant enrichment of arsenic in small sizes, and high recovery of vapor to ash.
- Due to the low concentration of arsenic in the vapor, no condensation is expected, due to the relatively high vapor pressure.

Parametric Tests

- Evaluate the effect of sulfur concentration and calcium on arsenic speciation.
- Run cases for the six coals described above.
- Use a single temperature profile a typical boiler.
 - Temperature varies from 2400-700 °F in 2.5 s.
 - 700 °F is a typical air preheater inlet temperature.
- Apply an average arsenic vaporization rate of 75% to all coals.
- Use the size and calcium distribution profiles for each coal from the "Toxics" report.

Parametric Results

- The effect of sulfur concentration is manifested in the small particle sizes.
 - The smaller sizes have a higher flux of arsenic and SO_2 due to the higher surface area.
 - The concentration dependence will follow a 1/d dependence (all else equal, e.g. CaO distribution).
- Higher sulfur concentrations result in higher vapor arsenic concentrations, and lower arsenic recovery to ash, as expected, due to lower CaO availability in high sulfur coals.