Schedule

- Mineral matter occurrence in coal (today)
- Ash transformation and deposition (Fri, June 5)
- Nitrogen/NO_x (Mon, Jun 8)
- Industrial Scale (Wed, Jun 10)
- Student presentations (Fri, Jun 12)
- Final exam review – Andrew (Mon, Jun 15)
- **Final oral exam on Wednesday, June 17**

Mineral Matter Occurrence in Coal

1. Mineral matter greatly affects boiler design
2. Analytical Methods
   A. Chemical Fractionation
   B. SEM and related techniques
      - Principles of operation
      - Potential problems
      - Examples
3. General Occurrence
   A. Discrete minerals
      - Types
      - Examples
   B. Organically-Associated Cations
      - Types
   C. Cations dissolved in pore water
   D. Organic Sulfur
   E. Other

Why Study the Inorganic Contents of Coal

- A major component of coal
  - 6-23 wt%
- Behavior drives furnace design
  - "Of all the coal properties, coal mineral matter generally has the greatest effect on boiler design and operation"
- Deposition affects plant operation
  - Heat transfer reduced
  - Erosion and corrosion of equipment
  - Removal and disposal of residue

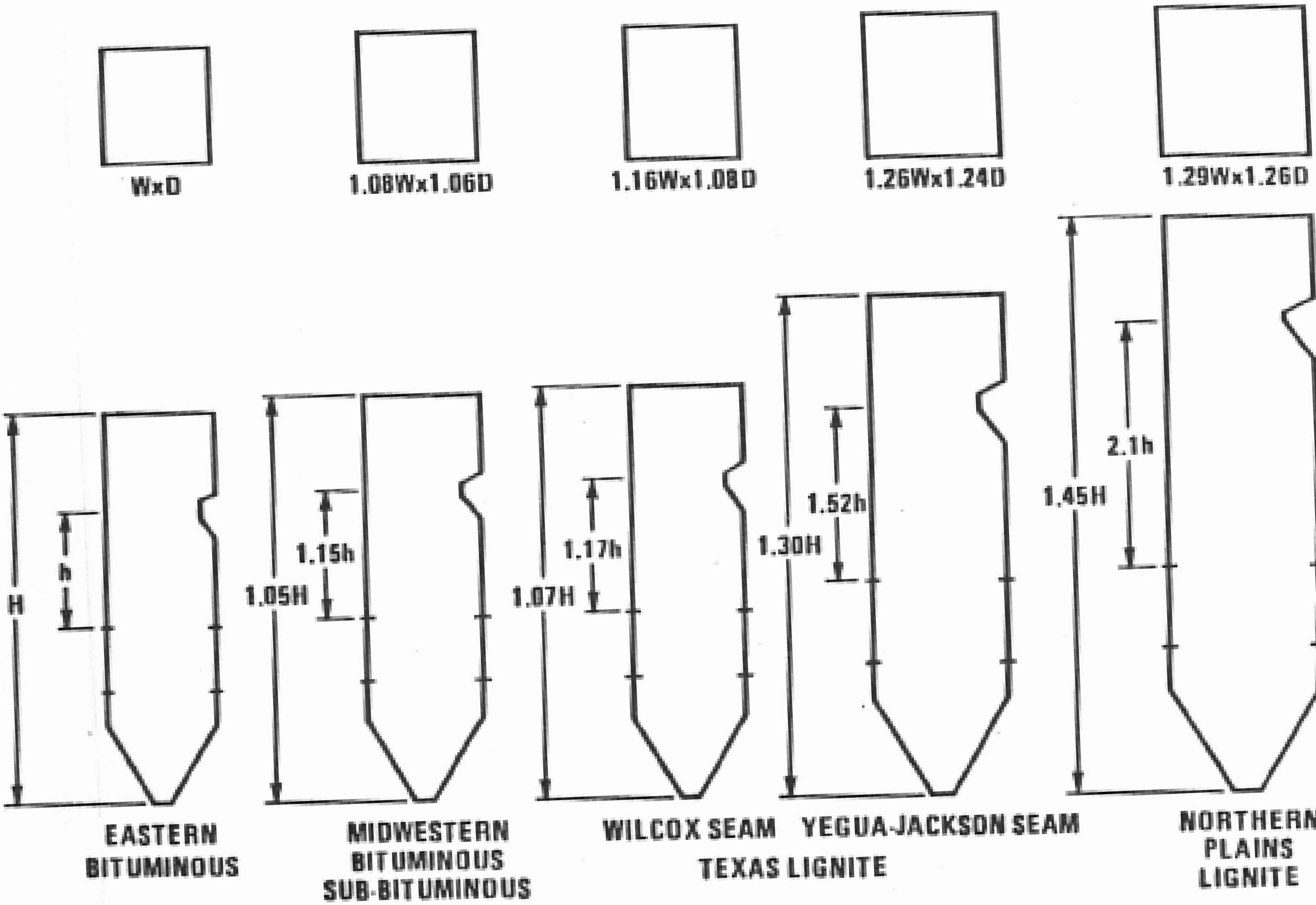


Figure 1. Effect of Coal properties on furnace size. Reproduced with permission from reference 11. Copyright 1978 C-E Publication.

Occurrence of Inorganics

- Discrete Minerals
- Organically-associated cations
- Cations dissolved in pore water
- Sulfur
  - Inorganic
  - Organic
- Other

Analysis Techniques

Chemical Analysis Methods

- High temperature ashing
- Low temperature ashing
- Chemical fractionation
- Scanning electron microscopy/ microprobe analysis
- ICP (inductively coupled plasma)

ASTM Ashing

High Temperature

- Oxidation at 750°C
- Alters some inorganics
- Empirical correlations
- Average composition
  - AA (ICP)
  - X-Ray (XRF)

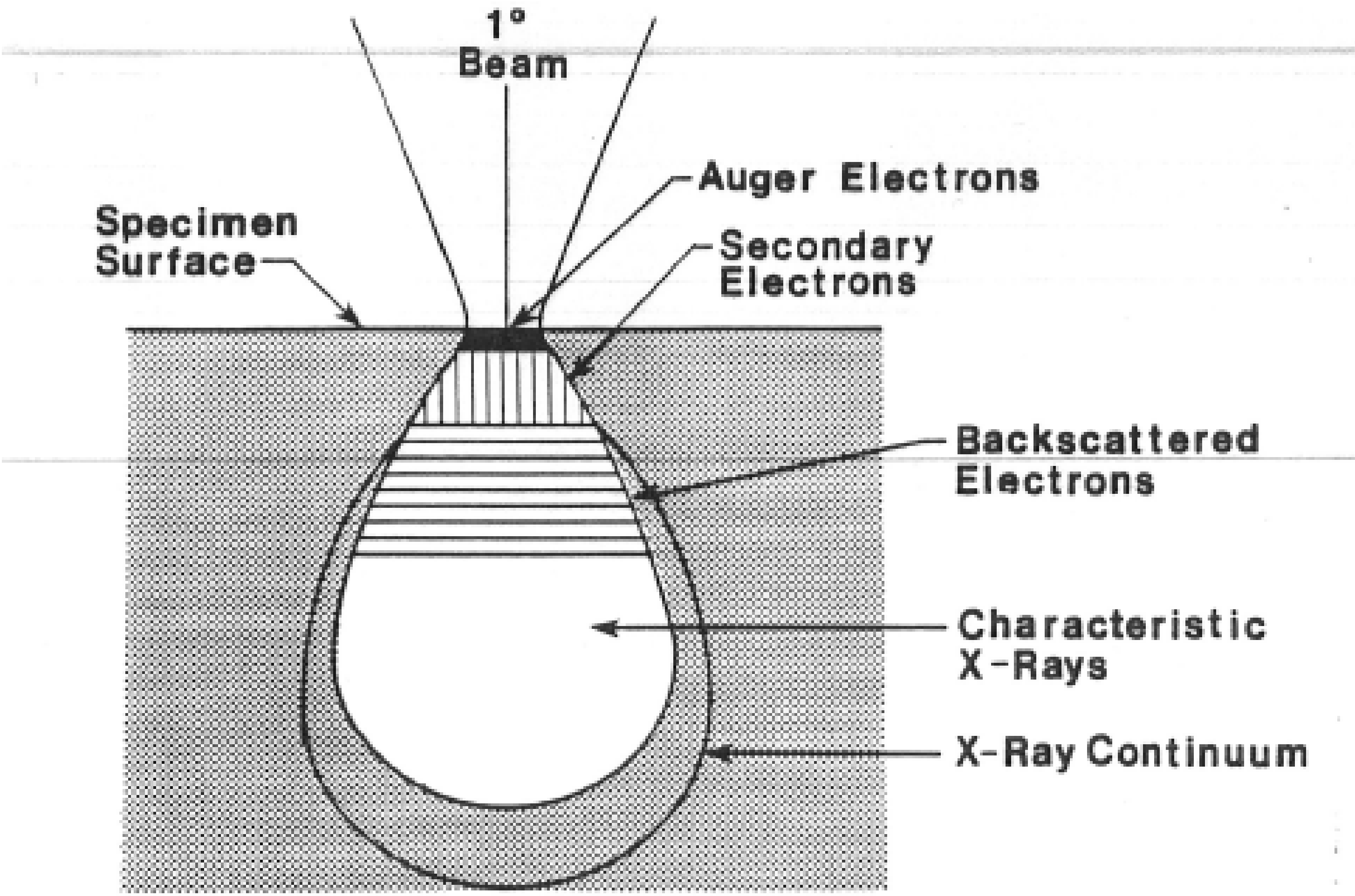
Low Temperature

- Oxidation in O_2 plasma
- Good for low rank coals
- Too slow for high rank coals
- Average composition

Scanning Electron Microscopy

- CCSEM – Identify and size discrete minerals
- EDAX – elemental analysis used to infer mineral species
- Can give included/excluded and association data
- Large number of analysis points required for statistically valid results

SEM



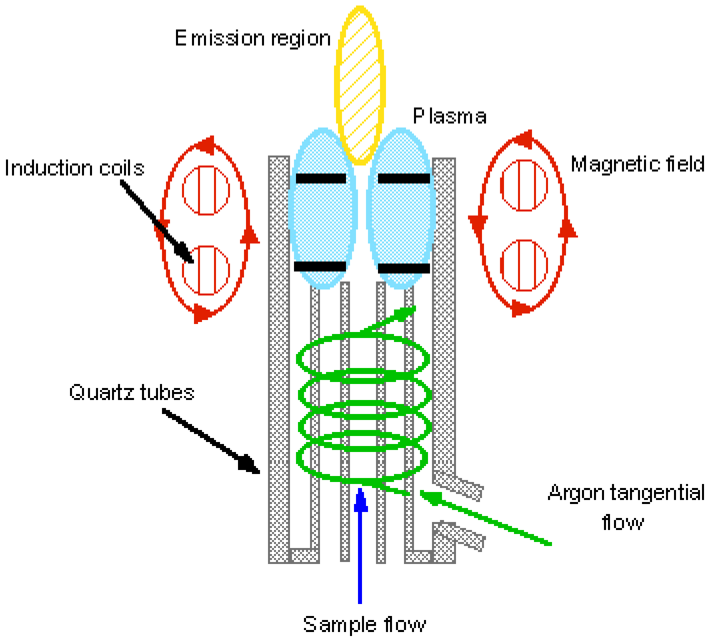
3-5. Cross section of the volume of primary excitation illustrating zones from which signals may be detected.

From Postek, M. T., K. S. Howard, A. H. Johnson, and K. L. Michael, Scanning Electron Microscopy: A Student's Handbook

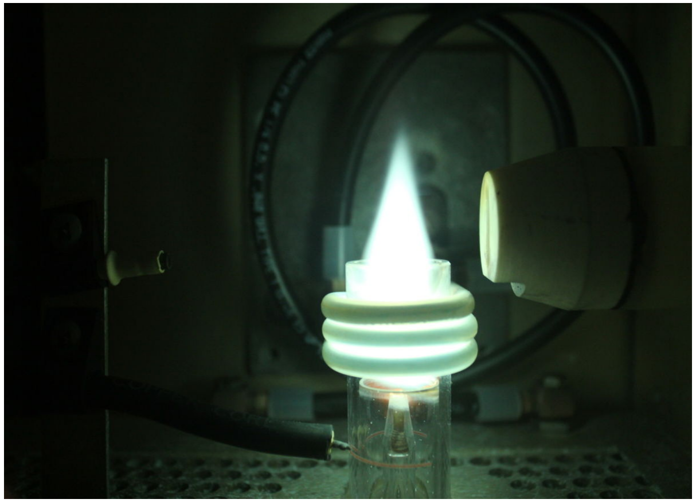
ICP

- Fully ash the sample (no carbon)
- Dissolve sample in acid with lithium borate flux ($Li_2B_4O_7$)
  - Need sample to be totally dissolved
- Inject liquid spray through plasma (10,000 K)
  - Ash reverts to elements
- During rapid cool down, look at atomic adsorption spectra

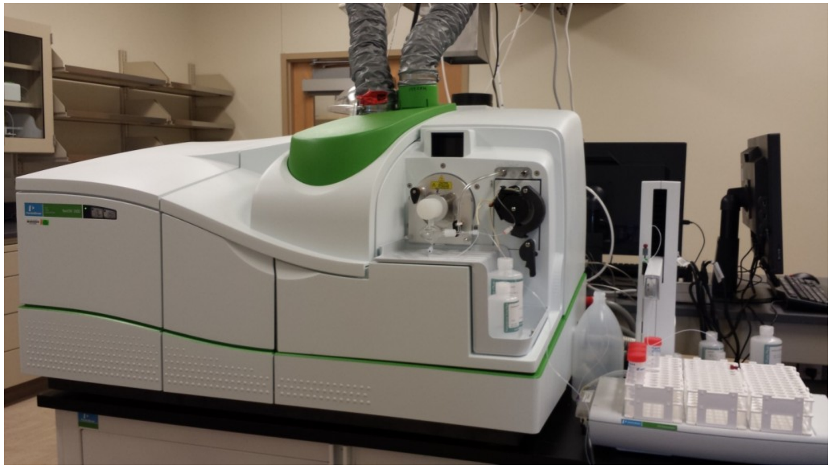
ICP schematic



http://elchem.kaist.ac.kr/vt/chem-ed/spec/atomic/emission/icp.htm



https://en.wikipedia.org/wiki/Inductively_coupled_plasma



http://www.jcesr.org/edl/analytical-electrochemistry-lab/inductively-coupled-plasma-mass-spectrometry-icp-ms/

Question 1

- Please describe the CCSEM technique for mineral characterization.

CCSEM

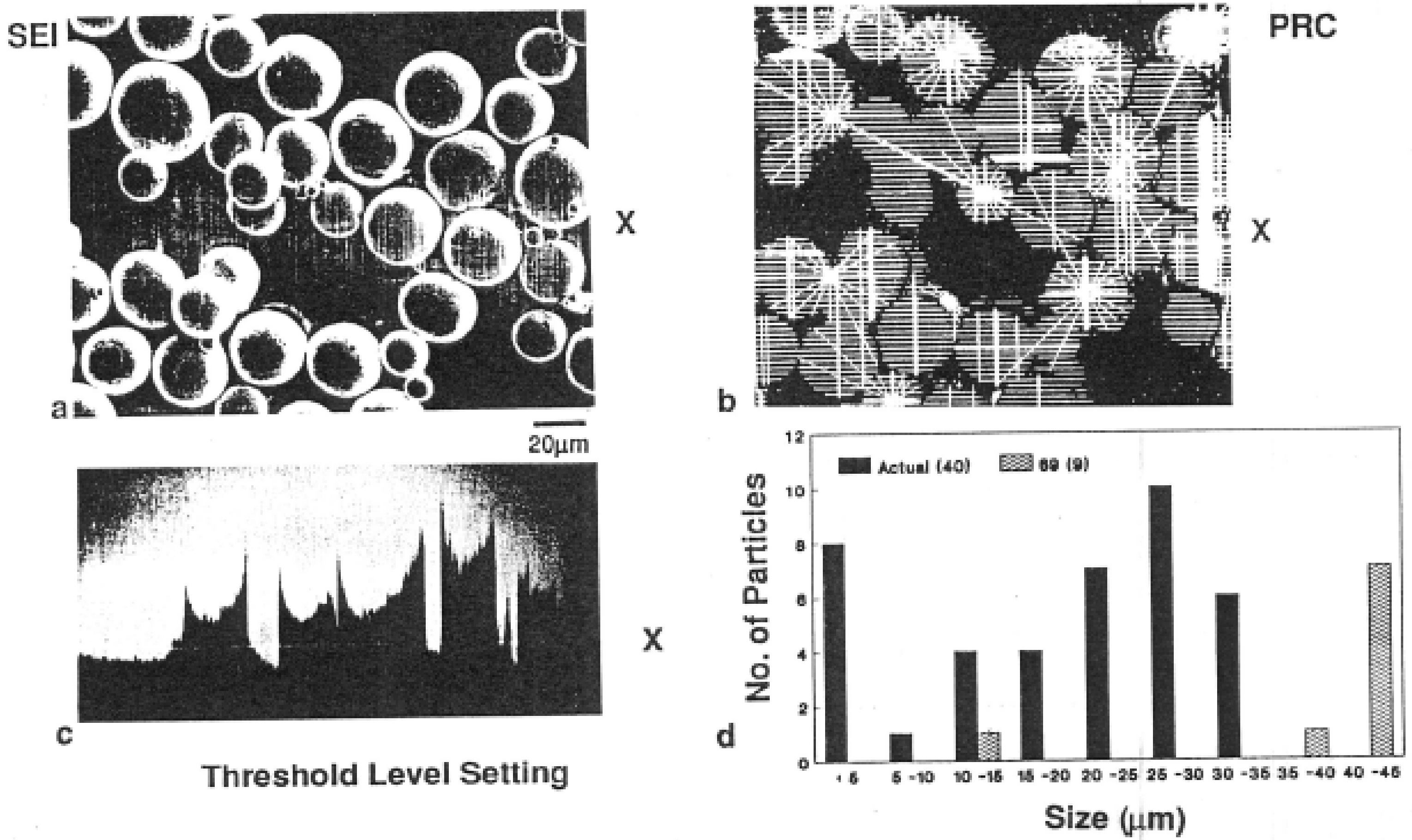
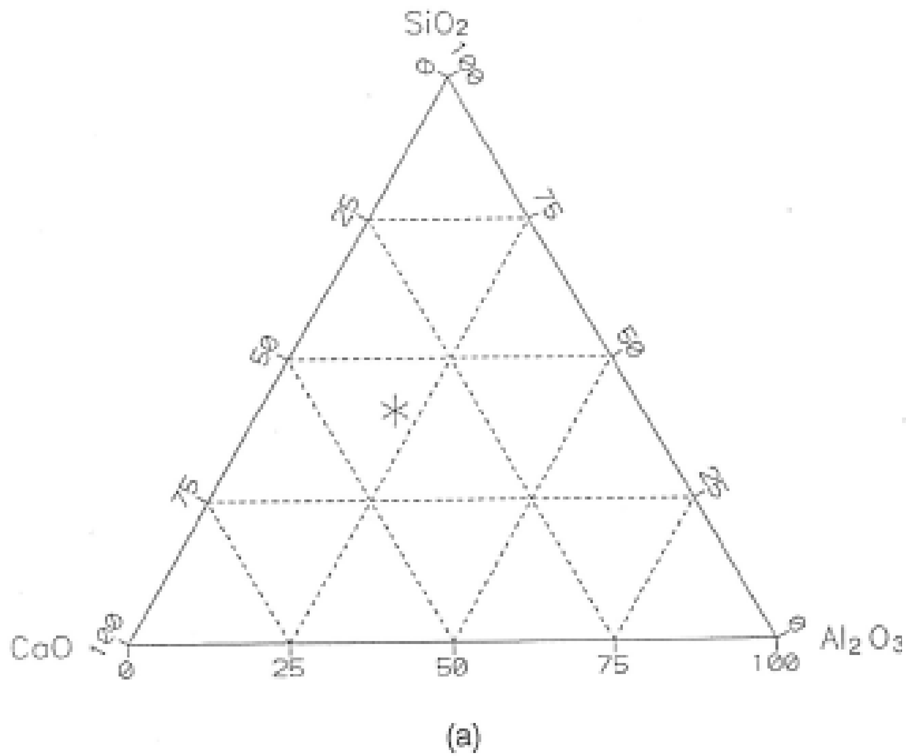
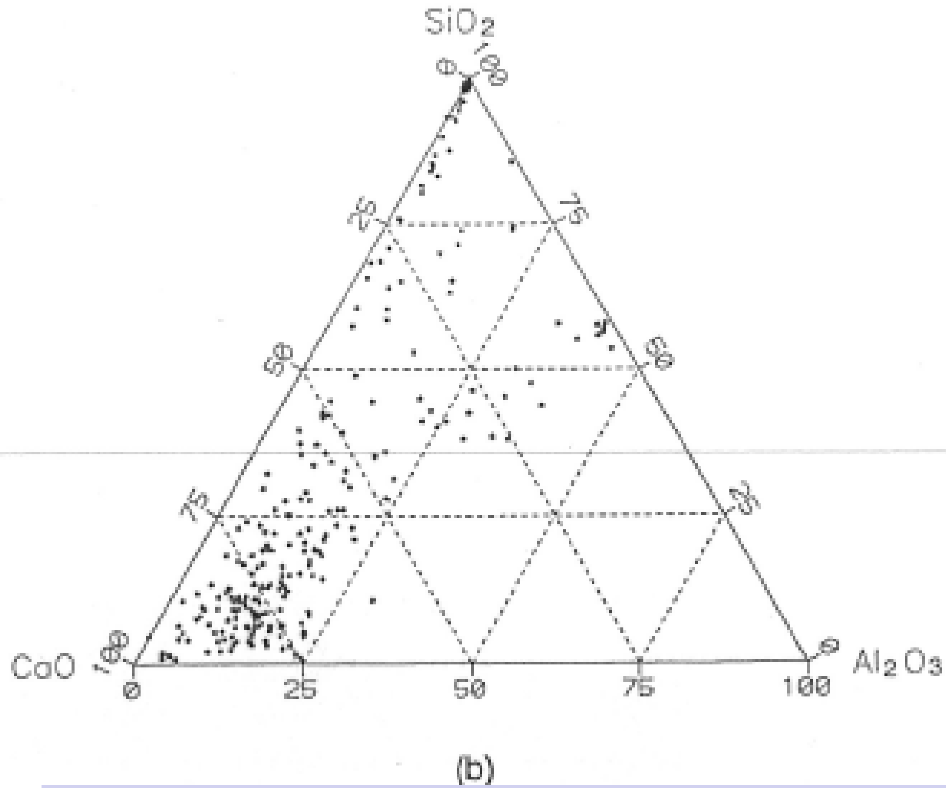


Figure 3.3 Illustration of: (a) the secondary electron image of a Pd-Rh particles; (b) the PRC image of the same sample; (c) the waveform, with the threshold level arbitrarily set at 69 (arbitrary units); and (d) a histogram of the number of particle vs. particle size as determined by the CCSEM and as determined manually. Compare with Fig. 3.4.

Question 2. Coal Ash Analysis





ASTM Bulk Analysis

CCSEM Analysis

Fig. 4.2 Chemical information in coal ash provided by various types of chemical analysis: (a) ASTM ash analysis, and (b) CCSEM analysis of fly ash.

Table 5-5. Definitions of Inorganic Particle Types. Values are Percents of the Total X-ray Counts for the Elements of Interest.

Quartz	Al<5, Si≥80
Iron Oxide	Si<10, S<5, Mg<5, Al<5, Fe≥80
Aluminosilicate	K<5, Ca<5, Fe<5, Si>15, Al>15, Si+Al≥80
Ca Al-Silicate	S<10, Ca>K, Ca>Fe, Ca>5, Al>10, Si>10, Ca+Al+Si≥80
Fe Al-Silicate	S<5, Fe>Ca, Fe>K, Fe>5, Si>10, Al>10, Fe+Al+Si≥80
K Al-Silicate	K≥Ca, K≥Fe, K≥5, Si≥10, Al≥10, K+Si+Al≥80
Ankerite	S≤15, Mg<Fe, Fe≥20, Ca>20, Ca+Fe+Mg≥80
Pyrite	Ca≤10, 10≤Fe<40, S≥10, Fe+S≥80
Gypsum	Ti+Ba<12, Si<10, S>20, Ca≥20, Ca+S≥80
Barite	Fe<10, Ca≤5, S≥20, Ba+S+Ti≥80
Gypsum/Barite	Fe<5, Ca≥5, Ba≥5, Ti≥5, S≥20, Ca+Ba+Ti+S≥80
Apatite	P≥20, Ca≥20, Ca+P≥80
Ca Silicate	Al≤10, S≤10, Si≥20, Ca≥14, Ca+Si≥80
Gyp/Al Silicate	Al≥5, Si≥5, S≥5, Ca>5, Ca+S+Al+Si≥80
Ca Aluminate	S≤10, Si≤10, Al≥15, Ca≥20, Ca+Al≥80
Spinel	Ca<5, Si<5, Al≥5, Al+Mg+Fe≥80
Alumina	Al≥80
Calcite	S<10, Mg<5, Si<5, P<15, Ti<5, Ba<5, Ca>80
Rutile	S<5, Ti + Ba≥80
Dolomite	Mg>10, Ca>10, Ca+Mg≥80
Pyrrhotite/$FeSO_4$	10≤S<40, Fe+S≥80
KCl	K≥30, Cl≥30, K+Cl≥80
Ca Rich	65≤Ca<80
Si Rich	65≤Si<80
Unknown	All other compositions

from Hurley's dissertation

Question 3

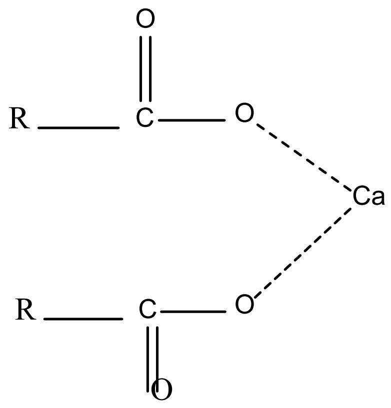
- What is the chemical fractionation technique for analyzing mineral matter, and why is it useful to industry? Please explain Table 4.1.

Chemical Fractionation

- Determines quantity of organically-bound inorganics
- Successive washing technique
  - Water – water solubles (e.g., salts)
  - Ammonium acetate – ion exchangeable
  - HCl – coordination complexes and acid solubles (e.g. carbonates)

Organically-Associated Cations

- Occur in low-rank (Western) coals
- Salts of carboxylic acids



- Na, Mg, Ca, K, Sr, Ba (Fe, Al)
- Up to 60% of total inorganics in some low rank coals

TABLE 4.1

Chemical Fractionation Results for the Four Low-Rank Coals

CHEMICAL FRACTIONATION[a] RESULTS FOR WYODAK (subC)

	Initial (μg/g mf coal)	Removed by H_2O (%)	Removed by NH_4OAC (%)	Removed by HCl (%)	Remaining (%)
Sodium	1,000	62	33	4	1
Magnesium	2,300	9	60	13	18
Aluminum	9,200	1	1	19	79
Silicon	12,600	1	1	1	97
Potassium	600	18	14	4	64
Calcium	10,800	4	34	39	23
Iron	7,800	0	0	44	56
Total % Inorganics Extracted		4	13	22	61

CHEMICAL FRACTIONATION RESULTS FOR BEULAH-ZAP (ligA)

	Initial (μg/g mf coal)	Removed by H_2O (%)	Removed by NH_4OAC (%)	Removed by HCl (%)	Remaining (%)
Sodium	6,900	26	66	1	7
Magnesium	3,870	1	73	22	4
Aluminum	9,460	1	0	10	89
Silicon	15,400	1	2	1	96
Potassium	168	16	53	3	28
Calcium	14,200	1	45	22	32
Iron	11,500	0	0	22	78
Total % Inorganics Extracted		7	34	11	48

CHEMICAL FRACTIONATION RESULTS FOR LOWER WILCOX (ligA)

	Initial (μg/g mf coal)	Removed by H_2O (%)	Removed by NH_4OAC (%)	Removed by HCl (%)	Remaining (%)
Sodium	300	55	36	9	0
Magnesium	2,200	6	80	14	0
Aluminum	24,100	1	0	4	95
Silicon	40,100	0	1	0	99
Potassium	500	39	31	2	28
Calcium	12,700	2	66	32	0
Iron	3,500	0	1	74	25
Total % Inorganics Extracted		1	13	10	76

CHEMICAL FRACTIONATION RESULTS FOR DIETZ (subB)

	Initial (μg/g mf coal)	Removed by H_2O (%)	Removed by NH_4OAC (%)	Removed by HCl (%)	Remaining (%)
Sodium	700	72	25	3	0
Magnesium	1,400	12	81	7	0
Aluminum	8,300	1	0	11	88
Silicon	12,100	1	2	1	96
Potassium	100	64	31	5	0
Calcium	5,000	4	70	26	0
Iron	1,500	0	1	99	0
Total % Inorganics Extracted		4	18	13	65

[a]Chemical fractionation is only used for low-rank coals and thus the higher-rank coals were not analyzed by this procedure.

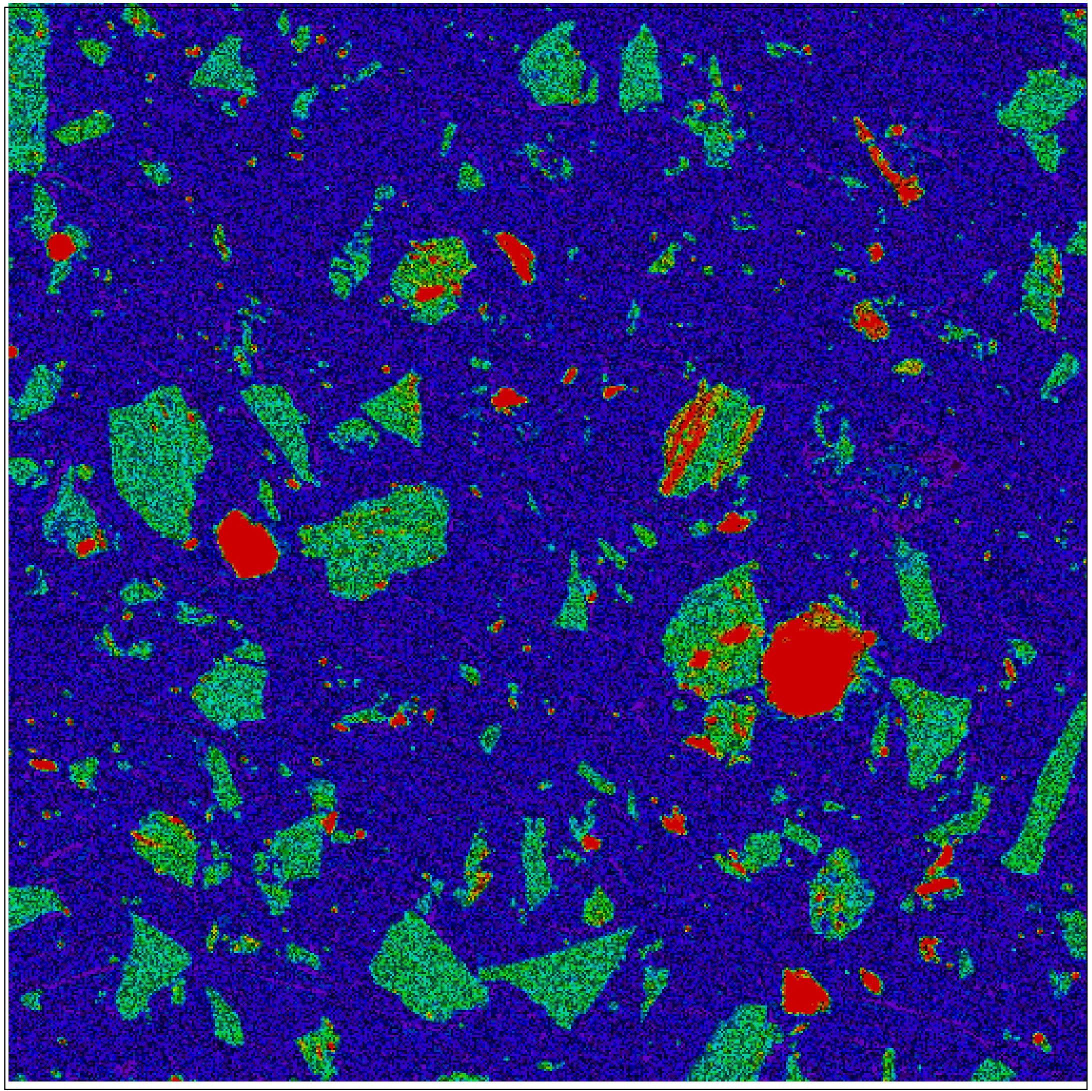
Question 4

- Explain what is meant by excluded versus included mineral grains, and why this may be important.

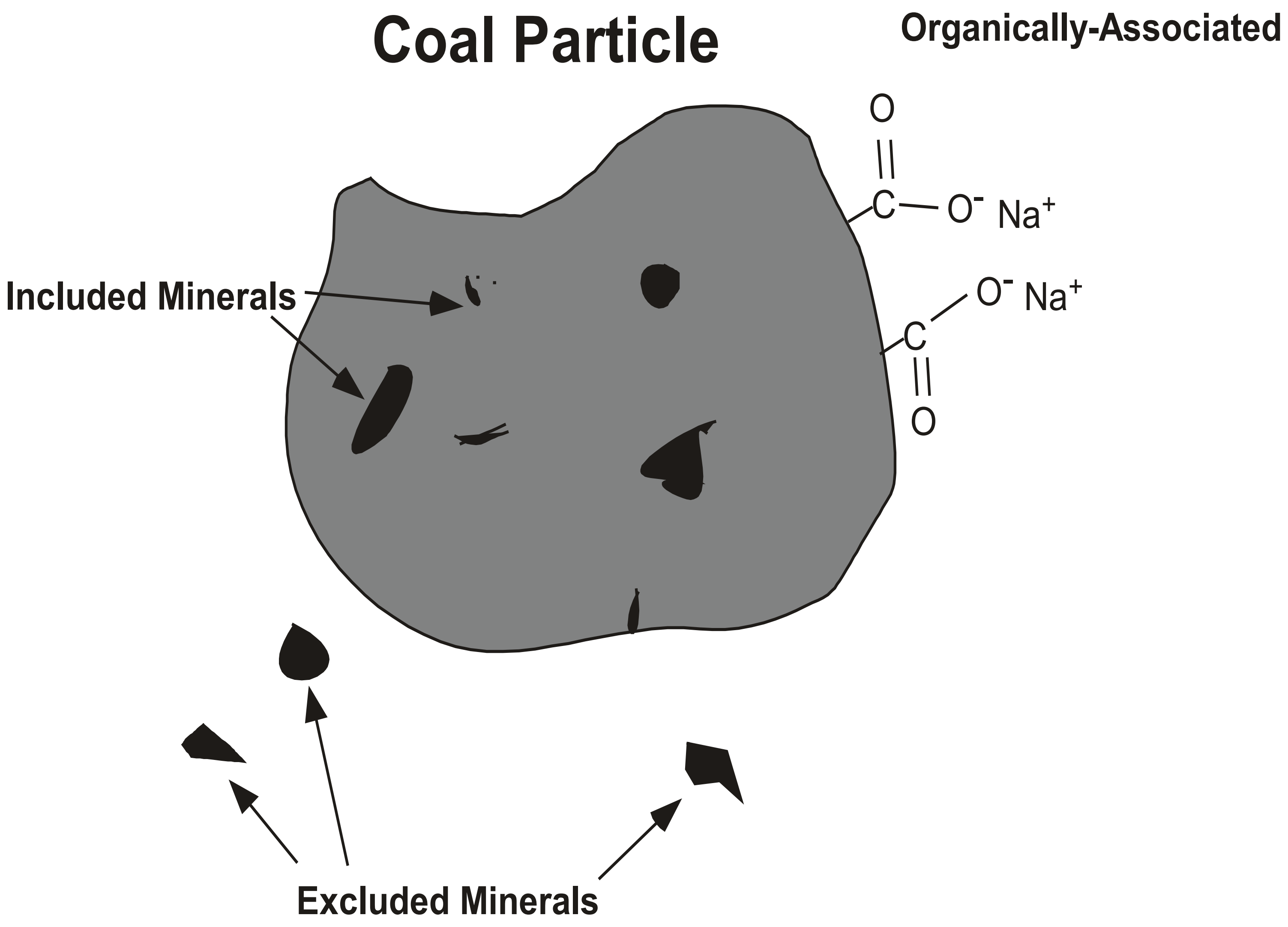
Discrete Minerals

- Small rocks in coal
- Included or excluded
- Major inorganic constituent
- Associations may play role in ash composition

CCSEM Image of a Kentucky#9 hv Bituminous Coal

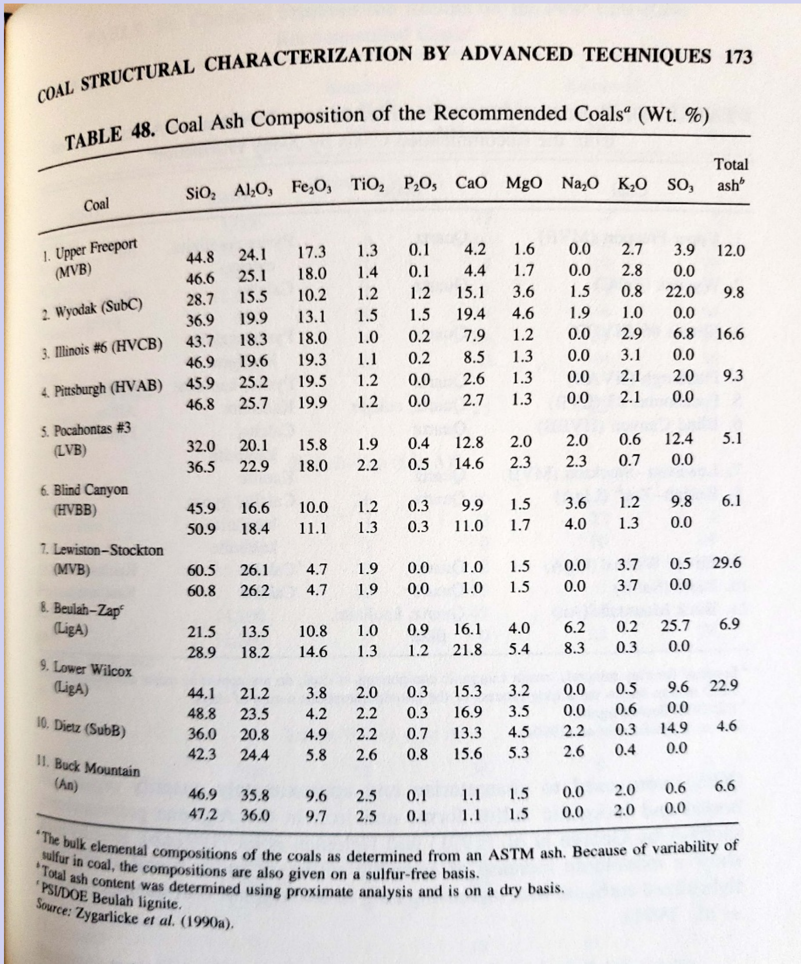


Types of Minerals



Question 5

- Calcium is one of the species that may cause low temperature fouling when there is sulfur present (CaSO4 is formed). Based on bulk Ca analysis only (see p. 173 of Lee Smith book), which coals have the highest low temperature fouling potential?
- In practice, only the low rank coals tend to exhibit the low temperature fouling. Why is there a discrepancy here?

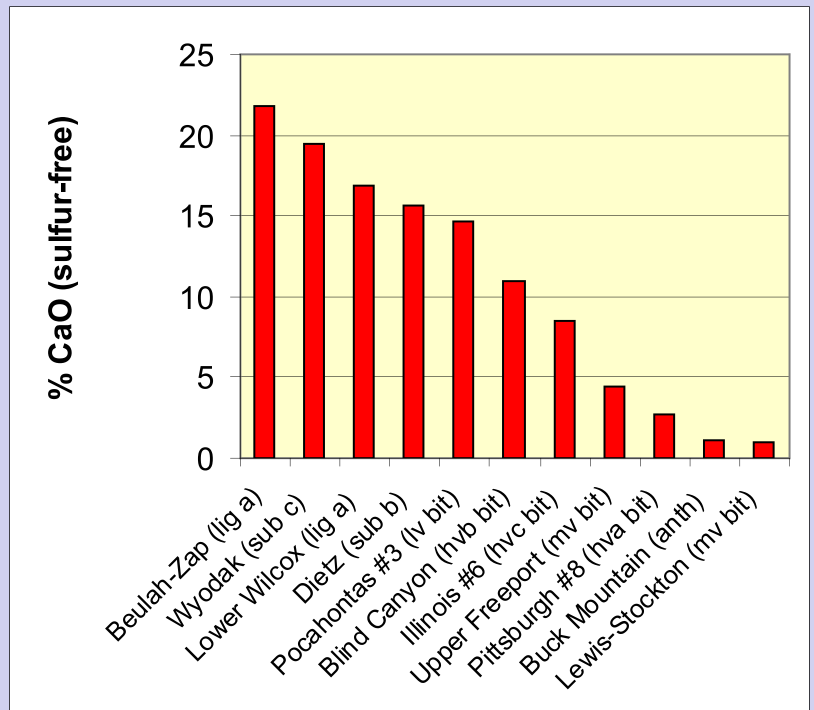


COAL STRUCTURAL CHARACTERIZATION BY ADVANCED TECHNIQUES 173

TABLE 48. Coal Ash Composition of the Recommended Coals[a] (Wt. %)

Coal	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	Na_2O	K_2O	SO_3	Total ash[b]
1. Upper Freeport (MVB)	44.8	24.1	17.3	1.3	0.1	4.2	1.6	0.0	2.7	3.9	12.0
	46.6	25.1	18.0	1.4	0.1	4.4	1.7	0.0	2.8	0.0	
2. Wyodak (SubC)	28.7	15.5	10.2	1.2	1.2	15.1	3.6	1.5	0.8	22.0	9.8
	36.9	19.9	13.1	1.5	1.5	19.4	4.6	1.9	1.0	0.0	
3. Illinois #6 (HVCB)	43.7	18.3	18.0	1.0	0.2	7.9	1.2	0.0	2.9	6.8	16.6
	46.9	19.6	19.3	1.1	0.2	8.5	1.3	0.0	3.1	0.0	
4. Pittsburgh (HVAB)	45.9	25.2	19.5	1.2	0.0	2.6	1.3	0.0	2.1	2.0	9.3
	46.8	25.7	19.9	1.2	0.0	2.7	1.3	0.0	2.1	0.0	
5. Pocahontas #3 (LVB)	32.0	20.1	15.8	1.9	0.4	12.8	2.0	2.0	0.6	12.4	5.1
	36.5	22.9	18.0	2.2	0.5	14.6	2.3	2.3	0.7	0.0	
6. Blind Canyon (HVBB)	45.9	16.6	10.0	1.2	0.3	9.9	1.5	3.6	1.2	9.8	6.1
	50.9	18.4	11.1	1.3	0.3	11.0	1.7	4.0	1.3	0.0	
7. Lewiston–Stockton (MVB)	60.5	26.1	4.7	1.9	0.0	1.0	1.5	0.0	3.7	0.5	29.6
	60.8	26.2	4.7	1.9	0.0	1.0	1.5	0.0	3.7	0.0	
8. Beulah–Zap[c] (LigA)	21.5	13.5	10.8	1.0	0.9	16.1	4.0	6.2	0.2	25.7	6.9
	28.9	18.2	14.6	1.3	1.2	21.8	5.4	8.3	0.3	0.0	
9. Lower Wilcox (LigA)	44.1	21.2	3.8	2.0	0.3	15.3	3.2	0.0	0.5	9.6	22.9
	48.8	23.5	4.2	2.2	0.3	16.9	3.5	0.0	0.6	0.0	
10. Dietz (SubB)	36.0	20.8	4.9	2.2	0.7	13.3	4.5	2.2	0.3	14.9	4.6
	42.3	24.4	5.8	2.6	0.8	15.6	5.3	2.6	0.4	0.0	
11. Buck Mountain (An)	46.9	35.8	9.6	2.5	0.1	1.1	1.5	0.0	2.0	0.6	6.6
	47.2	36.0	9.7	2.5	0.1	1.1	1.5	0.0	2.0	0.0	

[a] The bulk elemental compositions of the coals as determined from an ASTM ash. Because of variability of sulfur in coal, the compositions are also given on a sulfur-free basis.
[b] Total ash content was determined using proximate analysis and is on a dry basis.
[c] PSI/DOE Beulah lignite.
Source: Zygarlicke *et al.* (1990a).



Question 6

- Please explain the differences between the top and bottom figures in Figure 4.3.

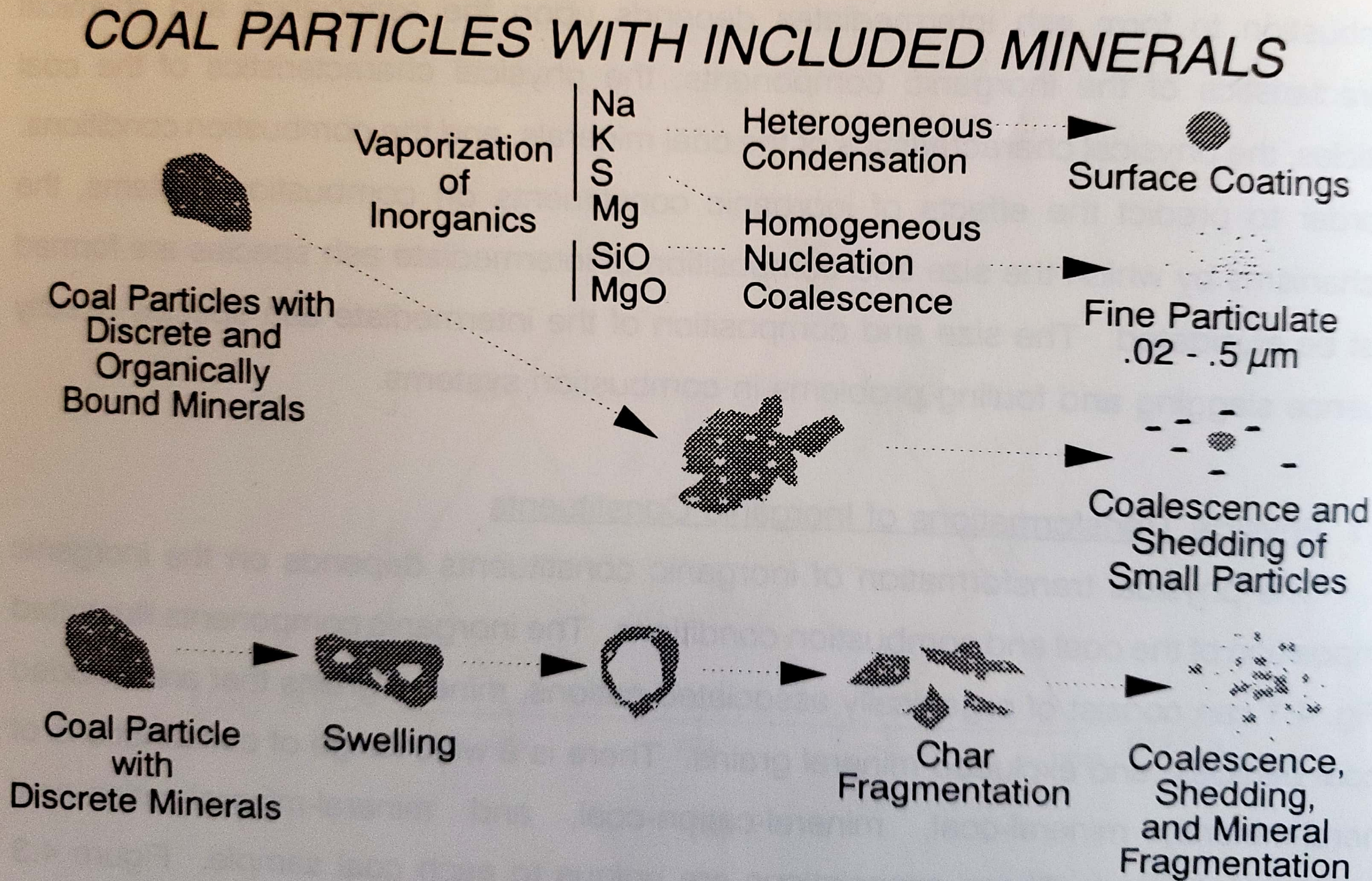

COAL PARTICLES WITH INCLUDED MINERALS
Vaporization of Inorganics
Na
K
S
Mg
SiO
MgO
Heterogeneous Condensation
Surface Coatings
Homogeneous Nucleation Coalescence
Fine Particulate .02 - .5 μm
Coal Particles with Discrete and Organically Bound Minerals
Coalescence and Shedding of Small Particles
Coal Particle with Discrete Minerals
Swelling
Char Fragmentation
Coalescence, Shedding, and Mineral Fragmentation

Fig 4.3 (top)

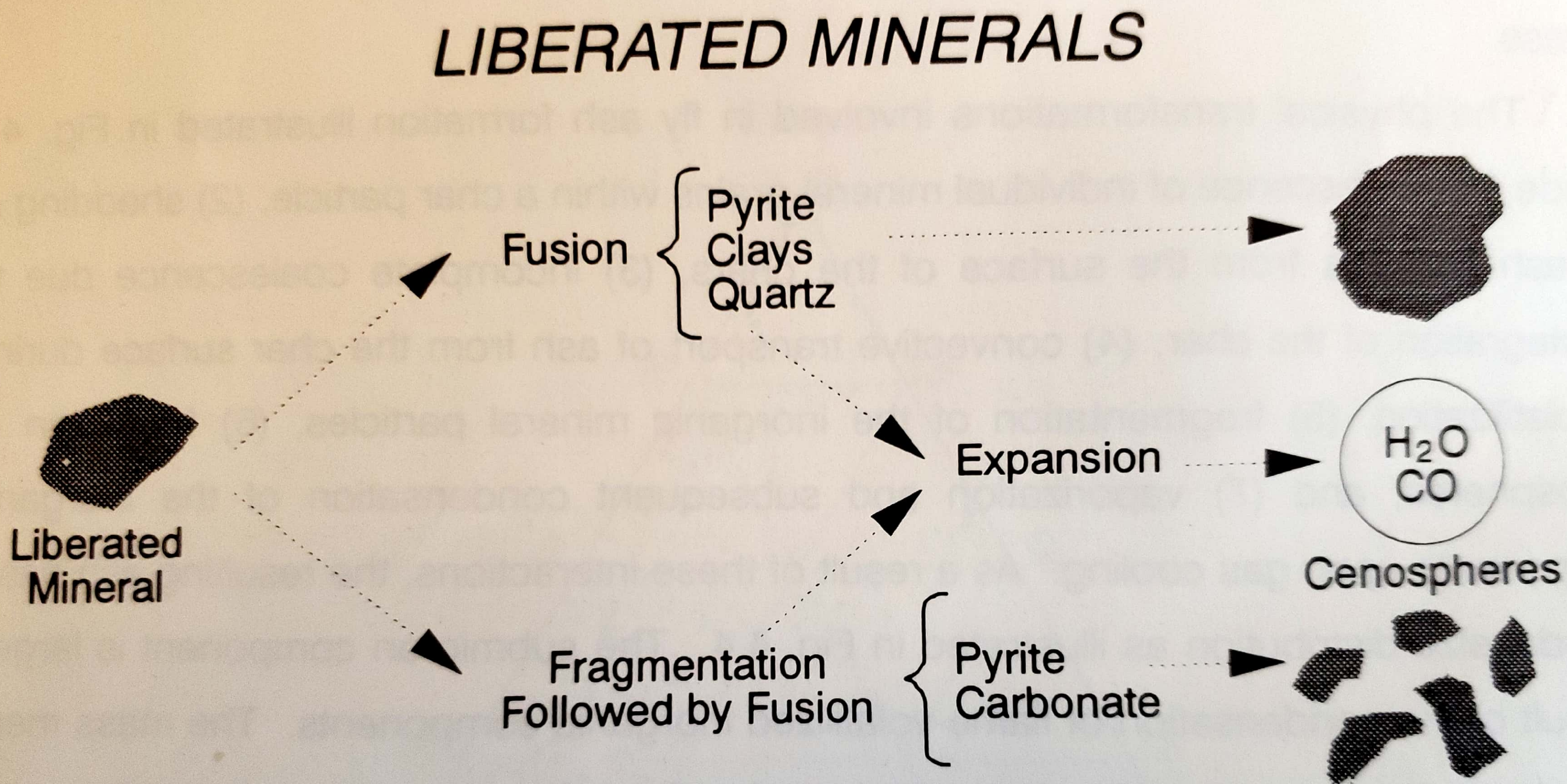


Fig. 4.3 Schematic diagram of the transformations of inorganic constituents during coal combustion.

TABLE 30

EXCLUDED/INCLUDED ANALYSIS OF MINERAL GRAINS FOR UTAH BLIND CANYON

MINERAL TYPES	% EXCLUDED	% INCLUDED
Quartz	65	35
Aluminosilicate	68	32
Fe-Aluminosilicate	33	67
K-Aluminosilicate	73	27
Ca-Aluminosilicate	80	20
Iron Oxide/Siderite	57	43
Pyrite	70	30
Calcite	68	32
Barite	33	67
Gypsum	63	37
Apatite	0	100
Dolomite	100	0
Gypsum/Aluminosilicate	40	60
Gypsum/Quartz	0	100
Ankerite	44	56
Aluminosilicate/Rutile	100	0
Aluminosilicate/Pyrite	100	0
Unknown	67	33
Quartz/Calcite	100	0
Quartz/Pyrite	0	100

TABLE 31

EXCLUDED/INCLUDED ANALYSIS OF MINERAL GRAINS FOR ILLINOIS #6

MINERAL TYPES	% EXCLUDED	% INCLUDED
Aluminosilicate	57	43
Gypsum/Aluminosilicate	20	80
Barite	100	0
Calcite	68	32
Ca-Aluminosilicate	33	67
Fe-Aluminosilicate	50	50
Gypsum	46	54
Gypsum/Quartz	25	75
Iron Oxide/Siderite	33	67
K-Aluminosilicate	46	54
Pyrite	51	49
Aluminosilicate/Pyrite	43	57
Py-Quartz/Pyrite	38	62
Quartz	47	53
Quartz/Calcite	100	0
Unknown	50	50

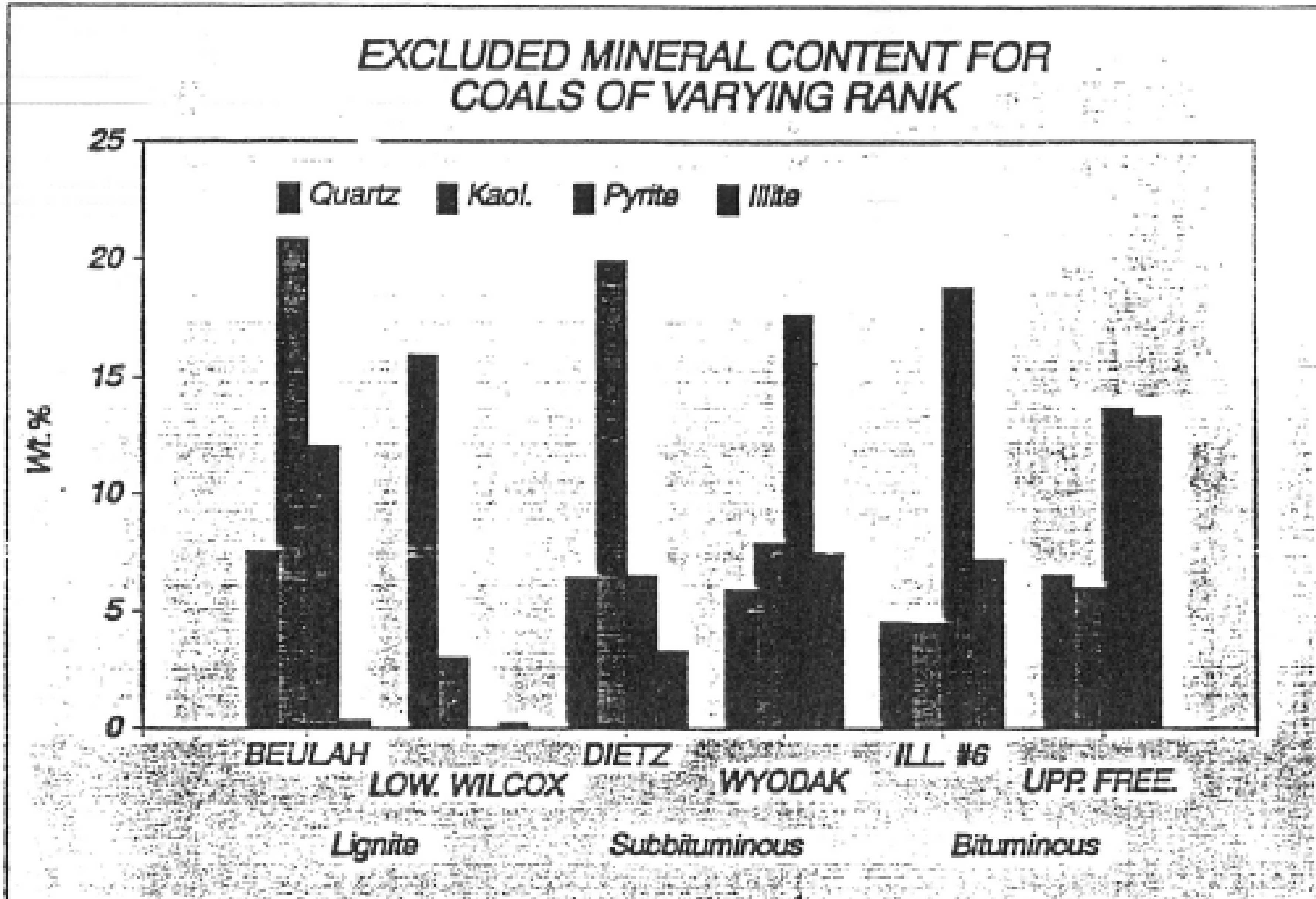
TABLE 10
MINERAL CONTENT IN EACH SIZE RANGE FOR UTAH BLIND CANYON

SIZE (µm)	<2.2	2.2-4.6	4.6-10	10-22	22-46	>46	Total [a] wt% (minerals)	Total [b] wt% (coal)
Quartz	17.73	15.18	17.27	12.19	10.55	0.00	14.91	0.91
Iron Oxide	3.99	3.79	0.00	3.67	14.87	0.00	4.03	0.25
Aluminosilicate	22.37	27.09	21.24	21.90	15.39	100.00	22.45	1.37
Ca-aluminosilicate	0.33	0.00	0.00	0.90	0.67	0.00	0.29	0.02
Fe-aluminosilicate	1.01	0.67	2.16	0.75	1.81	0.00	1.34	0.08
K-aluminosilicate	14.69	14.75	16.67	21.77	14.00	0.00	16.50	1.01
Ankerite	0.58	1.26	0.00	1.39	1.01	0.00	0.78	0.05
Pyrite	6.76	12.44	22.94	13.53	4.88	0.00	14.41	0.88
Gypsum	9.17	2.46	3.93	1.54	0.51	0.00	3.16	0.19
Barite	0.20	0.00	0.00	0.00	1.57	0.00	0.23	0.01
Ca-Silicate	0.00	0.00	0.00	1.07	0.00	0.00	0.20	0.01
Aluminosil./Gypsum	0.70	0.30	0.00	0.11	0.00	0.00	0.17	0.01
Alumina	0.47	0.52	0.00	0.00	0.00	0.00	0.18	0.01
Calcite	6.94	3.83	4.14	8.25	24.50	0.00	7.76	0.47
Rutile	0.75	0.00	0.00	0.00	0.00	0.00	0.07	0.00
Dolomite	0.60	0.40	0.00	0.26	0.00	0.00	0.21	0.01
Ca-Rich	1.85	1.32	0.00	3.04	1.03	0.00	1.22	0.07
Si-Rich	3.91	3.29	9.67	4.21	5.70	0.00	5.87	0.36
Periclase	0.83	0.00	0.00	0.00	0.00	0.00	0.08	0.01
Unknown	7.13	12.67	1.97	5.39	3.50	0.00	6.14	0.37
TOTAL % MINERAL	9.86	26.53	31.99	18.14	13.22	0.26	100.00	6.09

[a] Mineral Basis
[b] Coal Basis

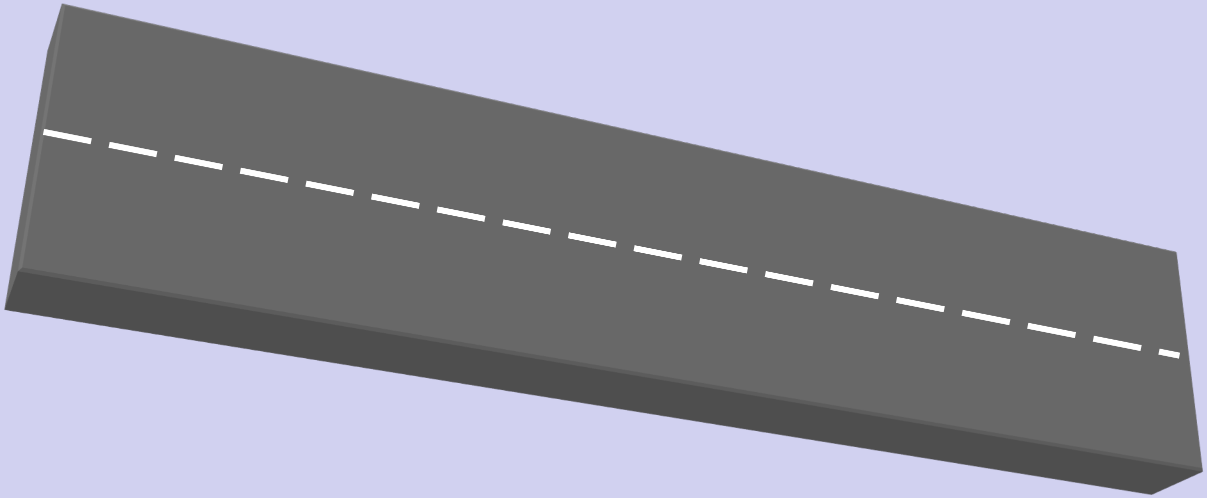
TABLE 11
PARTICLE-SIZE DISTRIBUTION OF INDIVIDUAL MINERALS FOR UTAH BLIND CANYON
(mineral basis)

SIZE (µm)	<2.2	2.2-4.6	4.6-10	10-22	22-46	>46
Quartz	11.7	27.0	37.1	14.8	9.4	0.0
Iron Oxide	9.8	25.0	0.0	16.5	48.8	0.0
Aluminosilicate	9.8	32.0	30.3	17.7	9.1	1.1
Ca-aluminosilicate	11.6	0.0	0.0	57.5	30.9	0.0
Fe-aluminosilicate	7.4	13.3	51.4	10.1	17.8	0.0
K-aluminosilicate	8.8	23.7	32.3	23.9	11.2	0.0
Ankerite	7.3	43.1	0.0	32.5	17.1	0.0
Pyrite	4.6	22.9	50.9	17.0	4.5	0.0
Gypsum	28.6	20.7	39.7	8.9	2.1	0.0
Barite	8.7	0.0	0.0	0.0	90.8	0.0
Ca-Silicate	0.0	0.0	0.0	100.0	0.0	0.0
Aluminosil./Gypsum	40.8	47.3	0.0	11.8	0.0	0.0
Alumina	25.1	74.9	0.0	0.0	0.0	0.0
Calcite	8.8	13.1	17.1	19.3	41.8	0.0
Rutile	100.0	0.0	0.0	0.0	0.0	0.0
Dolomite	27.6	49.5	0.0	22.4	0.0	0.0
Ca-Rich	14.9	28.7	0.0	45.2	11.1	0.0
Si-Rich	6.6	14.9	52.7	13.0	12.8	0.0
Periclase	100.0	0.0	0.0	0.0	0.0	0.0
Unknown	11.5	54.8	10.3	15.9	7.5	0.0


EXCLUDED MINERAL CONTENT FOR
COALS OF VARYING RANK
Quartz
Kaol.
Pyrite
Illite
Wt.%
25
20
15
10
5
0
BEULAH
LOW. WILCOX
DIETZ
WYODAK
ILL. #6
UPP. FREE.
Lignite
Subbituminous
Bituminous

Question 7

- The Delta power plant is going to sell all of their ash to UTA to serve as road filler for I-15. The roads are to be 50 feet wide and have an effective depth of 1.5 feet. The ash comprises 10% of the road fill. What length of road can be made using one year's accumulation of ash from this power plant? Assume 1000 MWe, 34% efficiency, 10% ash (dry basis), Utah bituminous coal.



Question 8

- Please find the range of melting points for the following compounds, and comment on how Na and Ca modify glass behavior in coal ash (look in CRC):
  - Sodium silicate ($Na_2Si_2O_5$)
  - Sodium sulfate (Na_2SO_4)
  - Silica (SiO_2)
  - Alumina (Al_2O_3)
  - Aluminum silicates
  - Calcium sulfate
  - Calcium aluminosilicates
  - Sodium aluminosilicates

Table 3.4 Silicate and oxide mineral species in coal

Species	Chemical formula	Specific[a] gravity (kg m^{-3})	Melting point (K)
	Silica and silicates—common occurrence		
Quartz	SiO_2	2650	1983
Kaolinite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$		2083
Muscovite	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	2900	(Mullite)
Illite	As muscovite with Fe, Ca, and Fe		
Montmorillonite	$(1-x)Al_2O_3 \cdot x(MgO,Na_2O) \cdot 4SiO_2 \cdot nH_2O$		
Chlorite	$Al_2O_3 \cdot 5(FeO,MgO) \cdot 3.5SiO_2 \cdot 7.5H_2O$		
Orthoclase	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	2500	
Plagioclase	$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$ —Albite		
	$CaO \cdot Al_2O_3 \cdot 2SiO_2$ —Anorthite		
	Silicates—less common occurrence		
Augite	$Al_2O_3 \cdot Ca(Mg,Fe,Al,Ti) \cdot 0.2SiO_2$		
Amphibole	Augite + Na,F,P	3100	
Biotite	$Al_2O_3 \cdot 6(MgO \cdot FeO) \cdot 6SiO_2 \cdot 4H_2O$	3100	
Granite	$Al_2O_3 \cdot 3(CaO,MgO,FeO,MnO) \cdot 3SiO_2$		
Epidote	$4CaO \cdot 3(Al,Fe)O_3 \cdot 6SiO_2 \cdot H_2O$	3350	
Kyanite	$Al_2O_3 \cdot SiO_2$	3550	2083 (Mullite)
Sanidine	$K_2O_3 \cdot Al_2O_3 \cdot 6SiO_2$	2570	
Straurolite	$Al_2O_3 \cdot FeO \cdot 2SiO_2 \cdot H_2O$		
Tourmaline	$Na(Fe,Mn)_3 \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 3BO \cdot 2H_2O$	3100	
Zircon	$ZrO_2 \cdot SiO_2$	4500	2825
	Oxides and hydrated oxides		
Rutile	TiO_2[b]	4200	2100
Mangetite	Fe_3O_4	5140	1865
Hematite	Fe_2O_3	5200	1840
Limonite	$Fe_2O_3 \cdot H_2O$	4300	675[c]
Diaspore	$Al_2O_3 \cdot H_2O$	3400	425[c]

[a]The specific gravity of silicate minerals is in the range of 2500 to 3500 kg m^{-3}; it increases with Al_2O_3/SiO_2 ratio and decreases with H_2O content. The silicates containing Na, K, Ca, Mg, and Fe do not have a definite melting point temperature (Chap. 9).

[b]With the exception of rutile, the oxide minerals rarely occur in coal.

[c]Denotes loss of water.

From Mineral Impurities in Coal Combustion, Raask

Table 3.5 Carbonate, sulfide, sulfate, phosphate, and chloride minerals in coal

Species	Chemical formula	Specific gravity (kg m^{-3})	Melting/decomposition temperature (K)
Carbonates			
Calcite	$CaCO_3$	2710	1200[b]
Aragonite	$CaCO_3$	2710	1150[b]
Dolomite	$CaCO_3 \cdot MgCO_3$	2850	1050[b]
Ankerite	$CaCO_3 \cdot FeCO_3$		1000[b]
Siderite	$FeCO_3$	3830	800[b]
Sulfides			
Pyrite	FeS_2	5000	1075[b]
Marcasite	FeS_2	4870	1075[b]
Pyrrhotite	FeS_x	4600	1300
Chalcopyrite	CuFeS	4100	1300
Melnikovite	FeS_2 + (As, FeS, H_2O)	~5000	1075[b]
Galena	PbS	7500	1370
Mispickel	$FeS_2 \cdot FeAs_2$	~5000	1075[b]
Sphalerite	ZnS		
Sulfates			
Barytes	$BaSO_4$	4500	1855
Gypsum	$CaSO_4 \cdot 2H_2O$	2320	1725
Kieserite	$MgSO_4 \cdot H_2O$	2450	1395[b]
Thenardite	Na_2SO_4	2680	1157
Mirabilite	$Na_2SO_4 \cdot 10H_2O$	1460	1157
Melanterite	$FeSO_4 \cdot 7H_2O$	1900	755[b]
Keramolite	$Al_2(SO_4)_3 \cdot 16H_2O$	1690	945[b]
Jarosite	$K_2SO_4 \cdot xFe_2(SO_4)_3$	2500	900[b]
Phosphates			
Apatite	$Ca_5F(PO_4)_3$	3100	>1500
Evansite	$3Al_2O_3 \cdot P_2O_5 \cdot 18H_2O$	2560	>1775
Chlorides			
Halite	NaCl	2170	1074
Sylvite	KCl	1980	1043
Bischofite	$MgCl_2 \cdot 6H_2O$	1570	987

[a]Calcite, dolomite, ankerite, siderite, pyrite, barytes, and apatite minerals occur frequently. Gypsum and other sulfates are found mainly in low-rank and weathered coals; other mineral species are rarely found.

[b]Denotes the decomposition temperature.

Mineral Content of Biomass

Question 9

Biomass fuels that contain significant amounts of potassium or chlorine cause significant corrosion problems. Based on potassium and chlorine contents, estimate which biomass fuels will cause corrosion problems. (Hint: try the Jenkins biomass paper)

Table 2
Compositions, heating values, and alkali index for selected fuels [1]

	Alfalfa stems	Wheat straw	Rice hulls	Rice straw	Switch-grass	Sugar cane bagasse	Willow wood	Hybrid poplar
Proximate analysis (% dry fuel)								
Fixed carbon	15.81	17.71	16.22	15.86	14.34	11.95	16.07	12.49
Volatile matter	78.92	75.27	63.52	65.47	76.69	85.61	82.22	84.81
Ash	5.27	7.02	20.26	18.67	8.97	2.44	1.71	2.70
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ultimate analysis (% dry fuel)								
Carbon	47.17	44.92	38.83	38.24	46.68	48.64	49.90	50.18
Hydrogen	5.99	5.46	4.75	5.20	5.82	5.87	5.90	6.06
Oxygen (diff.)	38.19	41.77	35.47	36.26	37.38	42.82	41.80	40.43
Nitrogen	2.68	0.44	0.52	0.87	0.77	0.16	0.61	0.60
Sulfur	0.20	0.16	0.05	0.18	0.19	0.04	0.07	0.02
Chlorine	0.50	0.23	0.12	0.58	0.19	0.03	< 0.01	0.01
Ash	5.27	7.02	20.26	18.67	8.97	2.44	1.71	2.70
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Elemental composition of ash (%)								
SiO_2	5.79	55.32	91.42	74.67	65.18	46.61	2.35	5.90
Al_2O_3	0.07	1.88	0.78	1.04	4.51	17.69	1.41	0.84
TiO_2	0.02	0.08	0.02	0.09	0.24	2.63	0.05	0.30
Fe_2O_3	0.30	0.73	0.14	0.85	2.03	14.14	0.73	1.40
CaO	18.32	6.14	3.21	3.01	5.60	4.47	41.20	49.92
MgO	10.38	1.06	< 0.01	1.75	3.00	3.33	2.47	18.40
Na_2O	1.10	1.71	0.21	0.96	0.58	0.79	0.94	0.13
K_2O	28.10	25.60	3.71	12.30	11.60	0.15	15.00	9.64
SO_3	1.93	4.40	0.72	1.24	0.44	2.08	1.83	2.04
P_2O_5	7.64	1.26	0.43	1.41	4.50	2.72	7.40	1.34
CO_2 /other	14.80						18.24	8.18
Total	100.00	100.00	100.64	100.00	100.00	100.00	100.00	100.00
Undetermined	11.55	1.82	-0.64	2.68	2.32	1.39	8.38	1.91

From Jenkins et al paper

Higher heating value (constant volume)									
MJ/kg	18.67	17.94	15.84	15.09	18.06	18.99	19.59	19.02	
Btu/lb	8025	7714	6811	6486	7766	8166	8424	8178	
Alkali index (as oxide)									
(kg alkali/GJ)	0.82	1.07	0.50	1.64	0.60	0.06	0.14	0.14	
(lb alkali/MM Btu)	1.92	2.49	1.17	3.82	1.41	0.15	0.32	0.32	

	Almond shells	Almond hulls	Pist. shells	Olive pitts	Demol. wood	Yard waste	Fir mill	Mixed paper	RDF
Proximate analysis (% dry fuel)									
Fixed carbon	20.71	20.07	16.95	16.28	12.32	13.59	17.48	7.42	0.47
Volatile matter	76.00	73.80	81.64	82.00	74.56	66.04	82.11	84.25	73.40
Ash	3.29	6.13	1.41	1.72	13.12	20.37	0.41	8.33	26.13
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ultimate analysis (% dry fuel)									
Carbon	49.30	47.53	50.20	52.80	46.30	41.54	51.23	47.99	39.70
Hydrogen	5.97	5.97	6.32	6.69	5.39	4.79	5.98	6.63	5.78
Oxygen (diff.)	40.63	39.16	41.15	38.25	34.45	31.91	42.10	36.84	27.24
Nitrogen	0.76	1.13	0.69	0.45	0.57	0.85	0.06	0.14	0.80
Sulfur	0.04	0.06	0.22	0.05	0.12	0.24	0.03	0.07	0.35
Chlorine	< 0.01	0.02	< 0.01	0.04	0.05	0.30	0.19		
Ash	3.29	6.13	1.41	1.72	13.12	20.37	0.41	8.33	26.13
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Elemental composition of ash (%)									
SiO_2	8.71	9.28	8.22	30.82	45.91	59.65	15.17	28.10	33.81
Al_2O_3	2.72	2.09	2.17	8.84	15.55	3.06	3.96	52.56	12.71
TiO_2	0.09	0.05	0.20	0.34	2.09	0.32	0.27	4.29	1.66
Fe_2O_3	2.30	0.76	35.37	6.58	12.02	1.97	6.58	0.81	5.47
CaO	10.50	8.07	10.01	14.66	13.51	23.75	11.90	7.49	23.44
MgO	3.19	3.31	3.26	4.24	2.55	2.15	4.59	2.36	5.64
Na_2O	1.60	0.87	4.50	27.80	1.13	1.00	23.50	0.53	1.19

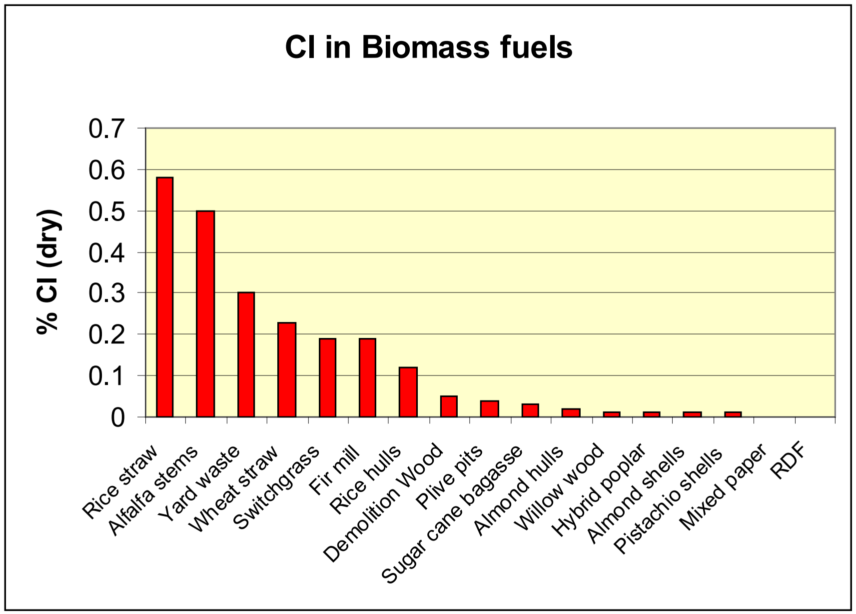
From Jenkins et al paper

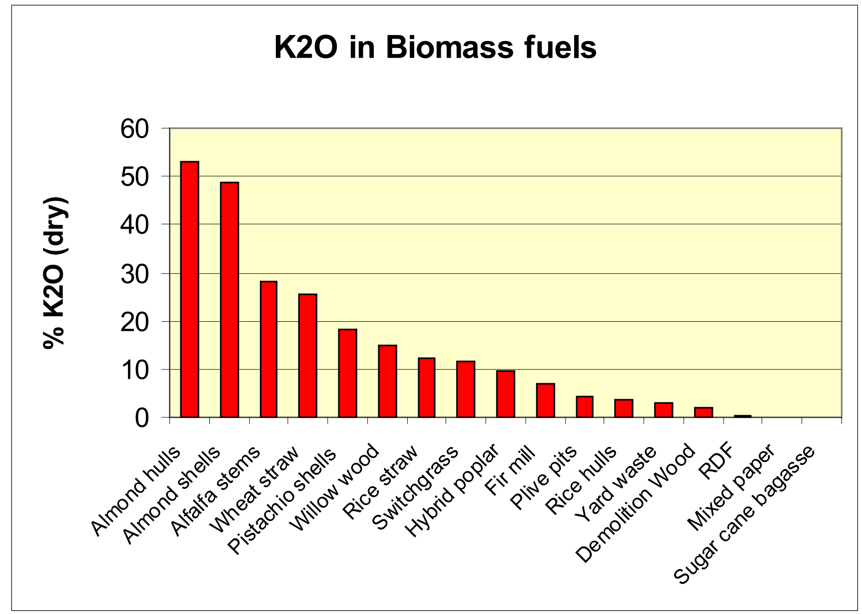
	Biomass power plant fuel blends						Coal (lvb)[a]	Lignite[b]
	Urban/ (1) Ag wood	Urban/ (2) Ag wood	Urban/ wood	Wood/ pit	Wood/ Al. hull	Wood/ Wheat straw		
Proximate analysis (% dry fuel)								
Fixed carbon	19.79	16.93	15.23	18.10	15.94	16.67	77.00	43.44
Volatile matter	75.89	80.57	79.23	76.77	77.28	75.14	18.49	42.95
Ash	4.32	2.50	5.54	5.13	6.78	8.19	4.51	13.69
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.08
Ultimate analysis (% dry fuel)								
Carbon	51.44	49.69	48.77	48.62	47.45	47.48	87.52	60.97
Hydrogen	5.67	5.87	5.76	5.78	5.53	5.81	4.26	4.07
Oxygen (diff.)	38.12	41.52	39.53	39.73	39.54	37.92	1.55	18.50
Nitrogen	0.41	0.33	0.27	0.65	0.59	0.35	1.25	1.02
Sulfur	0.03	0.04	0.07	0.06	0.08	0.12	0.75	1.81
Chlorine	0.01	0.05	0.06	0.03	0.03	0.13	0.16	0.04
Ash	4.32	2.50	5.54	5.13	6.78	8.19	4.51	13.69
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.10
Elemental composition of ash (%)								
SiO_2	39.96	28.81	55.12	52.55	45.60	55.50	37.24	20.93
Al_2O_3	12.03	8.47	12.49	13.15	10.75	9.37	23.73	13.78
TiO_2	0.87	0.83	0.72	0.43	0.54	0.50	1.12	0.41
Fe_2O_3	7.43	3.28	4.51	8.18	4.06	4.77	16.83	12.08
CaO	19.23	27.99	13.53	10.06	18.96	11.04	7.53	16.13
MgO	4.30	4.49	2.93	3.27	4.22	2.55	2.36	4.40
Na_2O	1.53	3.18	3.19	5.90	3.08	2.98	0.81	6.41
K_2O	5.36	8.86	4.78	5.04	6.26	6.40	1.81	0.22
SO_3	1.74	2.00	1.92	2.10	2.06	1.80	6.67	24.27
P_2O_5	1.50	2.57	0.88	1.90	1.47	1.04	0.10	0.00
CO_2 /other	6.05	6.07						
Total	100.00	100.00	100.07	100.00	100.00	100.00	98.20	98.63
Undetermined	0.00	3.45	−0.07	−2.58	3.00	4.05	1.80	1.37
Higher heating value (constant volume)								
MJ/kg	20.50	19.49	19.45	19.66	15.89	18.80	35.01	23.35
Btu/lb	8815	8379	8361	8450	6829	8083	15052	10040
Alkali index (as oxide)								
(kg alkali/GJ)	0.15	0.15	0.23	0.29	0.40	0.41	0.03	0.39
(lb alkali/MM Btu)	0.34	0.36	0.53	0.66	0.93	0.95	0.08	0.90

[a] Low volatile bituminous.

[b] See Ref. [13].

From Jenkins et al paper


Cl in Biomass fuels
% Cl (dry)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Rice straw
Alfalfa stems
Yard waste
Wheat straw
Switchgrass
Fir mill
Rice hulls
Demolition Wood
Plive pits
Sugar cane bagasse
Almond hulls
Willow wood
Hybrid poplar
Almond shells
Pistachio shells
Mixed paper
RDF


K2O in Biomass fuels
% K2O (dry)
60
50
40
30
20
10
0
Almond hulls
Almond shells
Alfalfa stems
Wheat straw
Pistachio shells
Willow wood
Rice straw
Switchgrass
Hybrid poplar
Fir mill
Plive pits
Rice hulls
Yard waste
Demolition Wood
RDF
Mixed paper
Sugar cane bagasse

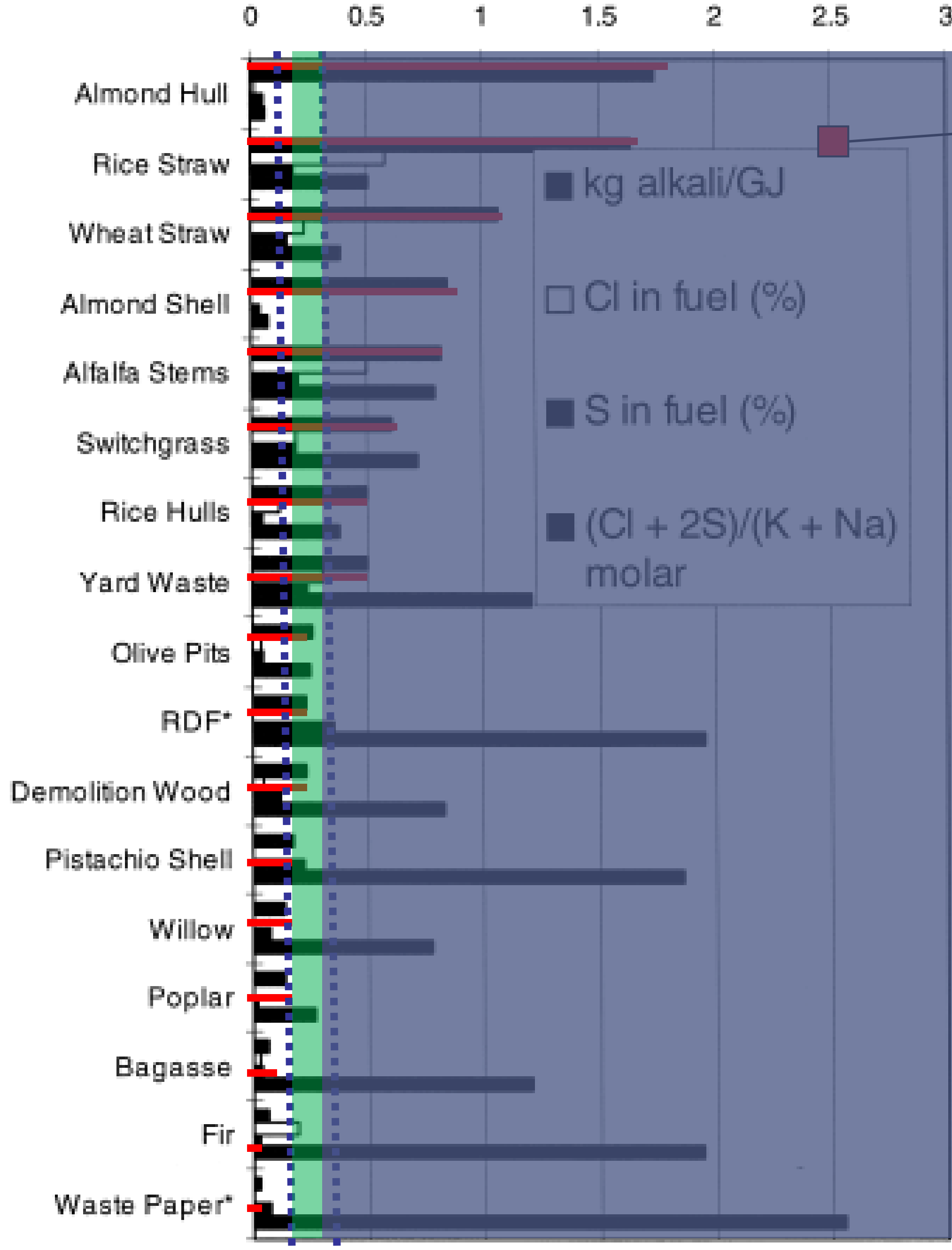


Fig. 9. Alkali index, chlorine and sulfur concentrations, and chloride–sulfate ratios for biomass.

K + Na

$$(1/Q)\,Y_{\mathrm{f}}^{\mathrm{a}}\left(Y_{\mathrm{K_2O}}^{\mathrm{a}} + Y_{\mathrm{N_2O}}^{\mathrm{a}}\right)$$

Alkali index > 0.17 Fouling likely

Alkali index > 0.34 Fouling certain

Q is the heating value on a dry basis (GJ/kg)

From Jenkins et al paper

What Did We Learn Today?

- Ash management is probably the most important design and operation criterion
- Mineral matter in coal is not one bulk composition
- Included vs excluded vs organically associated
- Lots of different minerals, wide range of melting points
- Ca, K and Na contents greatly affect fouling
- Ca, K, Na may be bound in glass-like minerals and therefore be almost inert