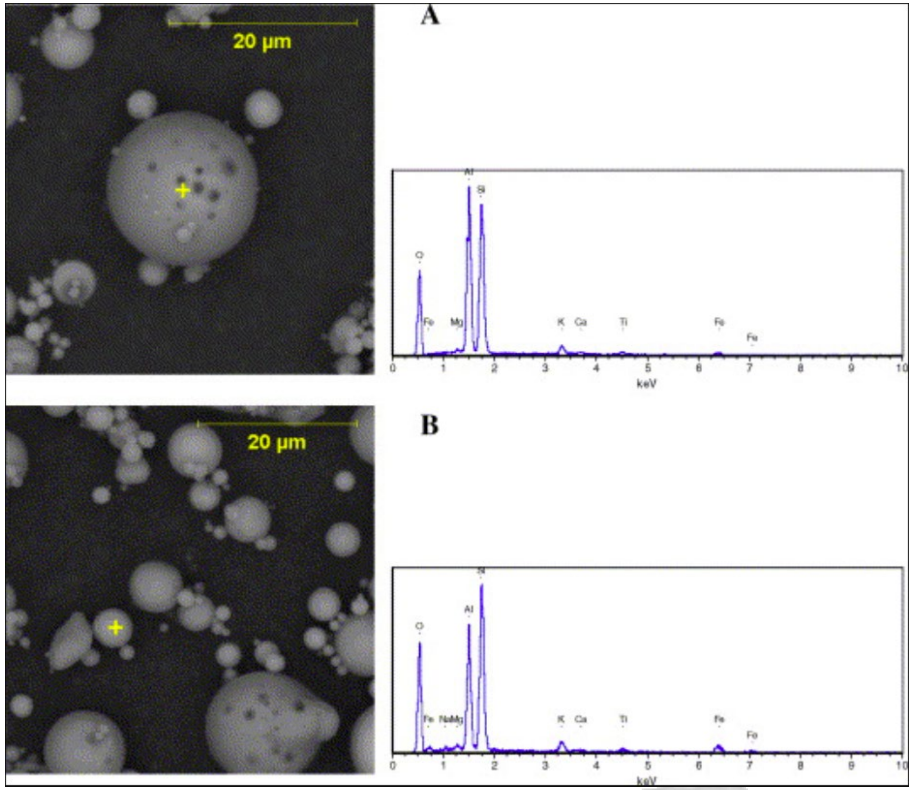
Chemical Engineering 733
Coal Combustion

Mineral Matter Discussion 1

05/24/22

Question 1: Please describe the CCSEM technique for mineral characterization

SEM – Scanning Electron Microscopy
EDS – Energy Dispersive X-ray Spectrometry



How time intensive is it to image a particle and then perform EDS?

Does the information from one particle provide statistically accurate information for the bulk ash or deposit?

B. Kutchko, A. Kim., Fly ash characterization by SEM-EDS. *Fuel*. 85 (17-18), 2537 – 2544.

Question 1: Please describe the CCSEM technique for mineral characterization

CCSEM – Computer Controlled Scanning Electron Microscopy

From Microbeam Technologies, Inc. Website (Steve Benson)

MTI uses computer-controlled scanning electron microscopy (CCSEM) to determine the size, composition, abundance, and association of mineral grains in prepared coal, biomass, and petroleum-coke samples. With this information, we can assess the behavior of the mineral grains during combustion or gasification. CCSEM analysis can also help us predict impacts of fuel properties on wear of system components, slag flow, fouling of heat exchangers, fine-particle collection, and ash handling.

From the Red Book, Page 305 - 306

In a typical CCSEM analysis, the electron beam is programmed to scan over the field of view and locate the bright inclusions that correspond to mineral species. On finding a bright inclusion, the beam performs eight diameter measurements of the inclusion, finds the center of the inclusion, and collects and energy-dispersive spectrum (EDS) at that point for two seconds. Software classifies the mineral grains based on published compositions of known minerals.

Subbituminous Coal	**Particle size, microns**						
MINERAL	1.0-2.2	2.2-4.6	4.6-10	10-22	22-46	46-400	TOTALS
QUARTZ	0.2	0.9	5.3	6.0	3.5	1.0	16.9
IRON OXIDE	0.0	0.0	1.0	1.3	0.1	0.0	2.4
PERICLASE	0.0	0.0	0.0	0.0	0.0	0.0	0.0
RUTILE	0.0	0.0	0.2	0.0	0.0	0.0	0.2
ALUMINA	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CALCITE	0.0	0.2	2.0	4.2	4.0	10.9	21.4
DOLOMITE	0.0	0.0	0.0	0.0	0.0	0.1	0.1
ANKERITE	0.0	0.1	0.1	0.0	0.0	0.0	0.2
KAOLINITE	0.3	1.4	6.0	6.0	2.4	1.1	17.2
MONTMORILLONITE	0.0	0.1	0.5	0.0	0.0	0.1	0.7
K AL-SILICATE	0.1	0.4	0.8	1.3	0.4	0.7	3.7
FE AL-SILICATE	0.0	0.0	0.1	0.0	0.0	0.0	0.1
CA AL-SILICATE	0.1	0.2	1.4	0.9	0.1	0.1	2.7
NA AL-SILICATE	0.0	0.0	0.1	0.0	0.0	0.0	0.2
ALUMINOSILICATE	0.0	0.1	0.2	1.0	0.1	0.0	1.4
MIXED AL-SILICA	0.0	0.1	0.1	0.0	0.0	0.0	0.3
FE SILICATE	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CA SILICATE	0.0	0.1	0.5	0.4	0.1	0.0	1.0
CA ALUMINATE	0.0	0.1	0.3	0.2	0.0	0.0	0.6
PYRITE	0.0	0.0	0.8	1.1	2.0	5.2	9.2
PYRRHOTITE	0.0	0.0	0.1	0.3	0.3	0.2	0.8
OXIDIZED PYRRHOTITE	0.0	0.0	0.2	0.0	0.3	0.1	0.6
GYPSUM	0.0	0.0	0.0	0.0	0.0	0.0	0.1
BARITE	0.0	0.1	0.2	0.0	0.3	0.2	0.8
APATITE	0.0	0.0	0.2	0.1	0.0	0.0	0.4
CA AL-P	0.0	0.0	0.0	0.0	0.0	0.0	0.0
KCL	0.0	0.0	0.0	0.0	0.0	0.0	0.0
GYPSUM/BARITE	0.0	0.0	0.0	0.0	0.0	0.0	0.0
GYPSUM/AL-SILICA	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SI-RICH	0.1	0.1	0.6	0.1	0.2	0.9	1.9
CA-RICH	0.0	0.2	0.3	0.5	0.1	1.8	3.0
CA-SI RICH	0.0	0.1	0.1	0.6	0.0	0.0	0.8
UNKNOWN	0.2	1.9	4.8	5.0	0.8	0.6	13.3
TOTALS	1.3	6.1	25.9	29.0	14.9	22.8	100.0

Question 1: Please describe the CCSEM technique for mineral characterization

- This information suggests that CCSEM can be a powerful tool to evaluate the nature of mineral matter in coal
- How might it be used to also classify ash and deposits?
- How might this information be useful in determining mechanisms of ash deposition?

Question 2: Please explain the ternary diagrams in Figure 4.2

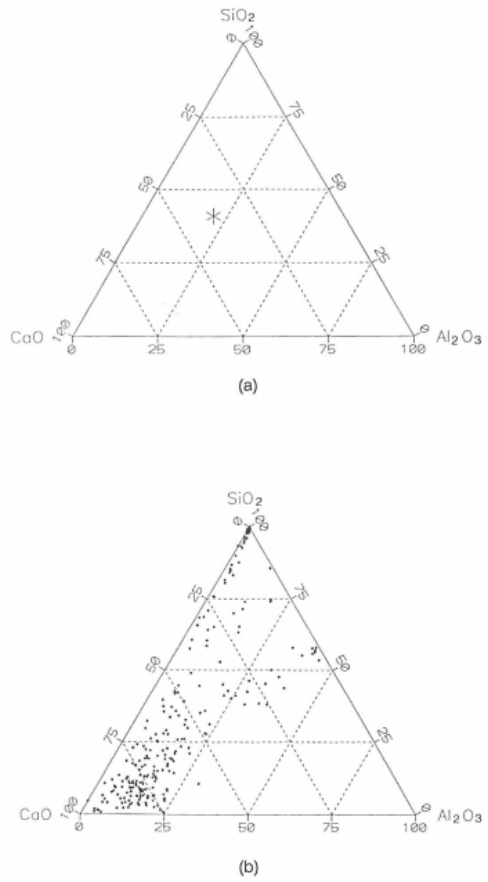


Fig. 4.2 Chemical information in coal ash provided by various types of chemical analysis: (a) ASTM ash analysis, and (b) CCSEM analysis of fly ash.

Typical method:

ICP/AAS – Inductively Coupled Plasma / Atomic Adsorption Spectrometry

ICP/MS – Inductively Coupled Plasma / Mass Spectrometry

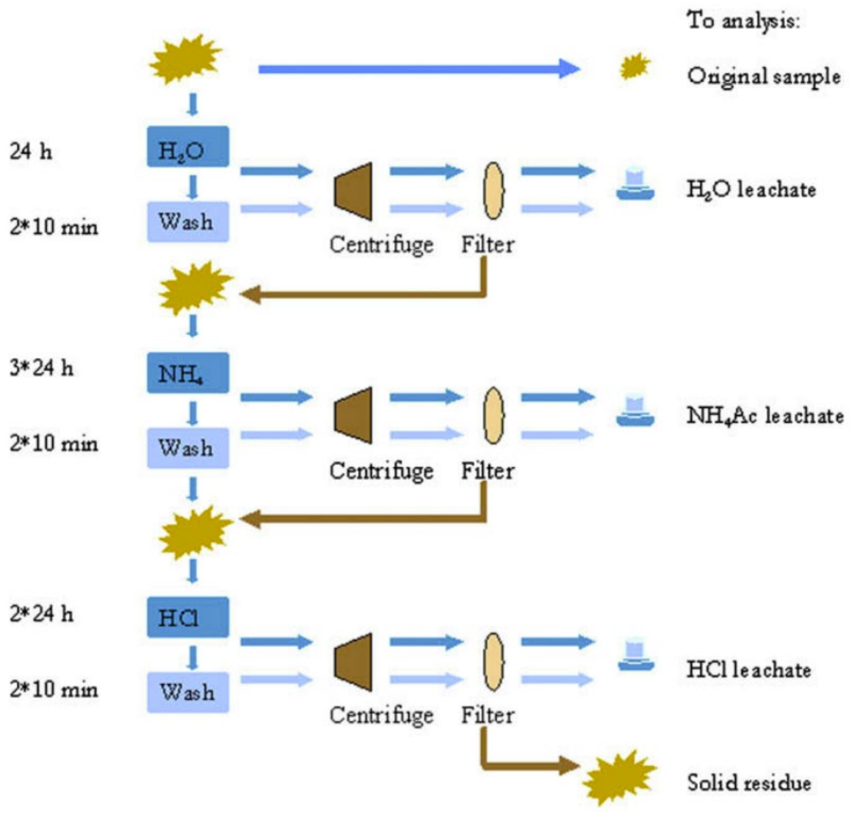
Sample is homogenized, vaporized then analyzed.

What other problems are there with this?

There is more information here, but is there something that is still missing?

Question 3: What is the chemical fractionation technique for analyzing mineral matter, and why is it useful to industry? Please explain Table 4.1.

1. Analyze original sample
2. Perform water extraction and analyze lechate
    1. Remove water soluble components
    2. Na in sodium sulfate, minerals associated with ground water
3. Perform acetate extraction and analyze lechate
    1. 1M ammonium acetate extraction
    2. Remove elements bound as salts or organic acids (ion exchangeable)
    3. Na, Ca and Mg
4. Perform acid extraction and analyze lechate
    1. 1M HCl extraction
    2. Remove hydroxides, oxides, carbonates, sulfates and organically coordinated species
    3. Fe, Ca
5. Analyze remaining solid
    1. Elements associated with clays, quartz and pyrite
    2. Silicates, oxides and sulfides



A. Petterson, L. Amand, B. Steenari., Chemical fractionation for the characterization of fly ashes from co-combustion of biofuels using different methods for alkali reduction. *Fuel*. 88, 1785 – 1772.

Question 3: What is the chemical fractionation technique for analyzing mineral matter, and why is it useful to industry? Please explain Table 4.1.

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.

How might this information be useful?

What would be the difference in fate between the water and acetate leached minerals and the residue minerals in the coal combustion process?

Hint: Elements in the remaining category are typically bound in such a way that inhibits vaporization.

Question 4: Explain what is meant by excluded versus included mineral grains, and why this may be important.

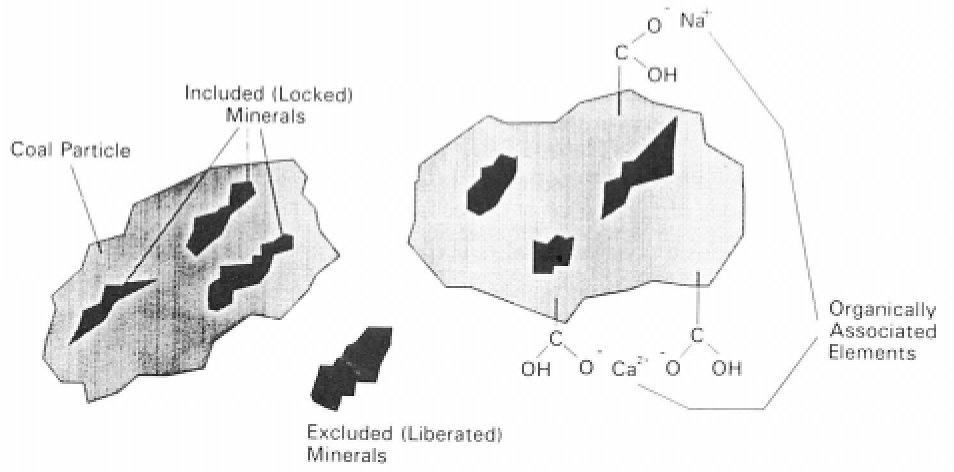


Fig. 4.1 Coal and associated inorganic components.

What could be the impact on mineral transformations during combustion?

What could be the impact on coal preparation?

How does this relate to the discussion about chemical fractionation?

Question 5: Calcium is one of the species that may cause low temperature fouling when there is sulfur present ($CaSO_4$ 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 coal tend to exhibit the low temperature fouling. Why is there a discrepancy here?

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).

1. Beulah – Zap (Lignite) @ 21.8
2. Wyodak (Sub. Bit.) @ 19.4
3. Lower Wilcox (Lignite) @ 16.9
4. Dietz (Sub. Bit) @ 15.6
5. Pocahontas #3 (Low Vol Bit.) @ 14.6
6. Illinois #6 (High Vol. Bit.) @ 8.5
7. Upper Freeport (Med. Vol. Bit.) @ 4.4
8. Pittsburgh (High Vol. Bit.) @ 2.7

Question 6: Please explain the differences between the top and bottom figures in Figure 4.3

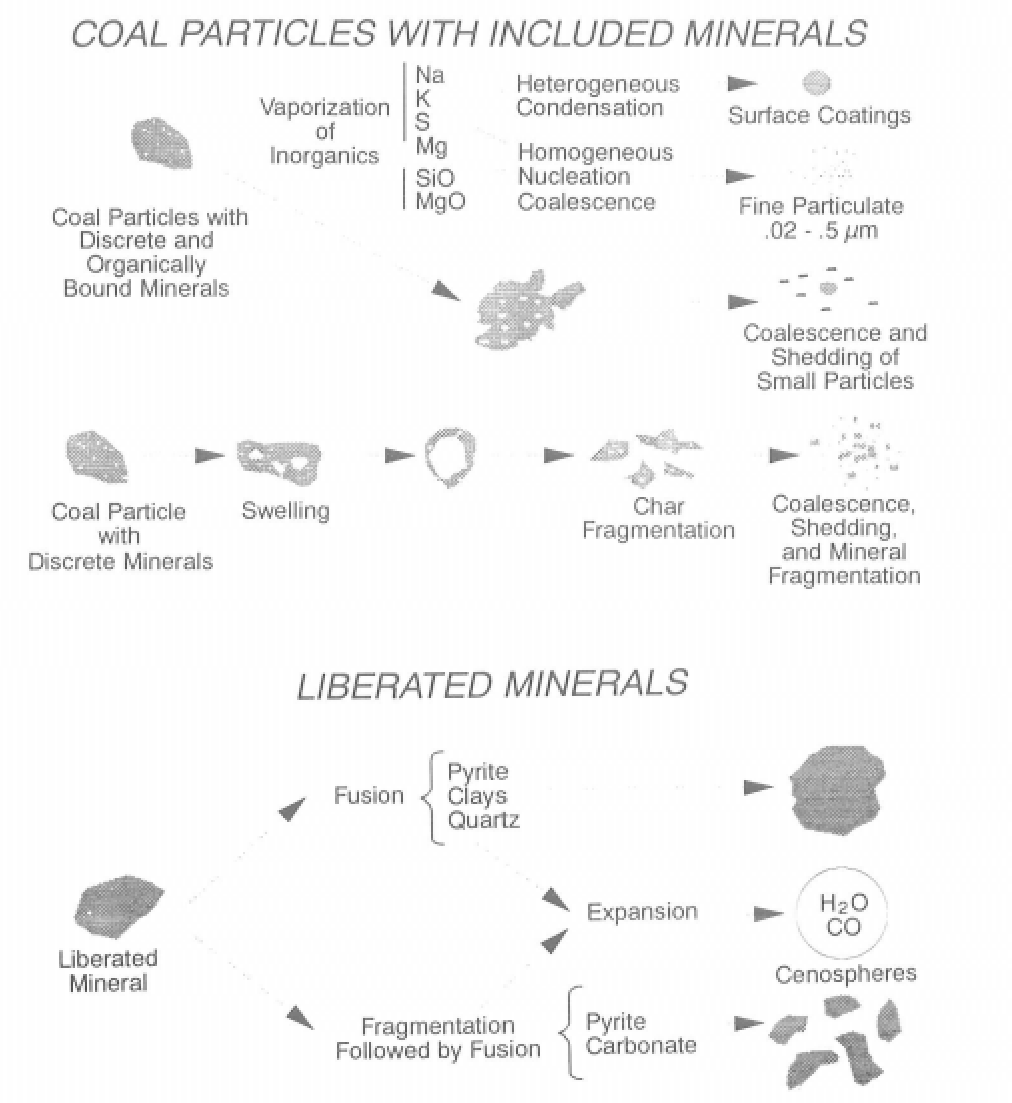


Fig. 4.3 Schematic diagram of the transformations of inorganic constituents during coal combustion.

How does this correspond to your understanding from chemical fractionation?

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. You may also assume that the specific gravity of concrete is 2.5.

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