θ	---	site coverage, the fraction of the active surface area that is covered by oxygen complexes
$\tau_{0.1}$	---	isothermal reactivity measurement, time for 10% burnoff
χ_b	---	mole fraction of bridgehead carbons
$\pounds$	---	a labile bridge
$\pounds^*$	---	highly reactive bridge intermediate
$\pounds_O$	---	initial fraction of labile bridges in the parent coal

Chapter 4

ASH FORMATION AND DEPOSITION

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4.1 INTRODUCTION

Ash deposition on heat-transfer surfaces has been examined for many years, resulting in voluminous literature on the subject. However, a precise and quantitative knowledge of the chemical and physical transformations of the inorganic components in coal during combustion has not been obtained due to the inability to quantitatively determine the inorganic composition of coal and to understand the complexity of the processes involved. At present, accurate prediction of the fate of the inorganic constituents during combustion as a function of coal composition and combustion conditions is not possible using currently accepted methods of analysis. For example, the composition of the coal ash produced under ASTM ashing conditions is used in most methods as an approximate guide to predict the behavior of inorganic constituents of a specific coal during combustion. This ashing technique can be used to predict average properties of the ash; however, examination of fly ash shows that many different types of particles are present, each having its own composition and probably its own melting behavior. Therefore, the behavior of individual fly ash particles may be very different from that predicted for the average ash composition.

The extent of ash-related problems depends upon the quantity and association of inorganic constituents in the coal, the combustion conditions, and the system geometry. The inorganic constituents are distributed within the coal matrix in several forms, including organically associated inorganic elements; coal-bound, included minerals; and coal-free, excluded minerals. The primary mineral groups that are found in all coals consist of clay minerals, carbonates, sulfides, oxides, and quartz. However, the specific types of inorganic components present depend upon the rank of the coal and the environment in which the coal was formed. For example, low-rank coals contain higher levels of

organically associated cations due to the high levels of oxygen that can act as bonding sites for various cations; approximately 25% of the oxygen is associated as carboxylic acid groups (refs. 1,2). In contrast, higher-ranked coals do not contain high levels of organically associated inorganic elements because of the lower oxygen levels.

During combustion, the inorganic materials are transformed into intermediate species which include gases, liquids, and solids. Studies of the final ash product (fly ash) indicate a bimodal size distribution (refs. 3-5). The smaller particles consist of submicron-size particles that form largely as a result of homogeneous condensation of flame-volatilized species. Flame-volatilized species may also condense heterogeneously on the surfaces of larger particles. The larger particles, sometimes referred to as residual ash, are largely derived from interactions between discrete mineral grains. In addition, organically associated elements also interact with mineral grains in lower-rank coals. Processes such as ash mineral coalescence, partial coalescence, ash shedding, char fragmentation and mineral fragmentation all play a role in determining the size and composition of the final fly ash.

Fireside deposition, fouling and slagging, occurs when intermediate ash species accumulate on heat transfer surfaces. The accumulation of ash particles depends upon the ability of the inorganic material to arrive at the heat transfer surface and to form strong bonds with the surface. Inorganic species are transported to the heat-transfer surfaces by several mechanisms depending on their size and physical state (ref. 6). The formation of a strong bond depends upon the physical and chemical characteristics of the steel surface, temperature of the steel surface, melting behavior of the ash particles, and the thermal and chemical compatibility of the deposit and steel surface (refs. 7, 8). Once a strongly bonded surface layer has accumulated, the temperature of the surface increases leading to more efficient collection of impacting ash particles. In addition, the deposited ash particles can react with gas phase inorganic species. Development of a low viscosity liquid phase may lead to increased deposit strength and the formation of a captive surface, resulting in rapid deposit growth (refs. 6, 9).

The development of strength in deposits at high temperatures (> 1200 K) is primarily due to viscous flow sintering which occurs when a thin liquid layer is formed between particles that tends to pull them together (ref. 10). The early stages of sintering (neck growth between particles) has been effectively described by Frenkel (ref. 11). The subsequent stages are described by two other models in the works of Mackenzie and Shuttleworth (ref. 12) and Scherer (ref. 13). Strength development at lower temperatures (< 1200 K) is due to condensation of flame volatilized species and gas solid interaction.

The ability of sintering to occur depends upon the temperature of the system, the reactivity of the deposited ash particles, the size distribution of the ash particles, and the gaseous environment in the vicinity of the deposit.

The chemical and physical characteristics of deposits found in utility boilers vary widely. In general, deposits range in consistency from being very heterogeneous consisting of pores, unreacted ash particles, a liquid phase matrix material, and crystalline material to a dense homogeneous non-crystalline slag. The type of liquid phases present in deposits is temperature-dependent due to the different thermal stability of the various chemical species. For example, some high temperature deposits contain high levels of liquid silicate phases that bond the deposit together, while lower temperature deposits are bonded by sulfate phases. Typically, the slagging deposits found in the radiant section of the utility boiler are more homogeneous as a result of assimilation of particles into a liquid phase. These deposits are primarily silicate-based, and the physical characteristics of the deposit are dictated by the physical and chemical properties of the liquid silicate phases. Iron-rich phases including silicates, sulfides, oxides and metallic iron also contribute to the formation of slag deposits. As temperatures decrease, the degree of assimilation or melting of the deposited material decreases. In addition, the participation of the silicate phases to bond the deposit together decreases. Two primary types of fouling deposits, which form in the convective pass of utility boilers, have been defined: high-temperature fouling, where silicates dominate, and low-temperature fouling, where sulfates dominate. In high-temperature fouling deposits, the bonding mechanism is primarily silicate, but some participation of sulfate bonding may occur at the deposit-tube interface. In low-temperature fouling, silicate-rich fly ash particles are present in the deposit, but are bonded together with sulfate-based phases.

A detailed quantitative understanding of the critical phenomena is necessary in order to develop models that will accurately predict ash deposition as a function of coal composition and combustion conditions. Several key areas are apparent from the above discussion:

1. The chemical composition and physical characteristics of inorganic components of coal. This information is essential since coal is a very heterogeneous and complex material.
2. The transformation mechanisms of inorganic coal components during combustion that result in the formation of inorganic vapors, liquids, and solids as a function of coal composition and combustion conditions. These transformations result in the formation of a bimodal-size distribution of ash particles having a wide range of chemical compositions.
3. The state (gas, liquid, and solid) and physical properties of the intermediate ash species as a function of temperature, atmosphere, and residence time.

These must be determined in order to predict ash transport and sticking efficiency.

4. The mechanisms of ash transport to heat-transfer surfaces as a function of ash particle size and aerodynamics/fluid dynamics.

5. The heat-transfer characteristics coupled with the reactivity and melting behavior of the deposited ash material.

6. The characteristics of the liquid phase components in the deposit with respect to deposit growth and strength development.

7. The physical characteristics of the deposit that influence its ability to be removed by conventional processes (*e.g.*, soot blowing and load drop).

The purpose of this chapter is to discuss the key issues related to ash formation and deposition in utility boilers firing pulverized coal, and to examine the development of quantitative mathematical models for prediction of ash behavior.

4.2 INORGANIC CONSTITUENTS IN COALS

The inorganic components in coals have been referred to as mineral matter, minerals, inherent/extraneous ash, and other names by many individuals that work with coal. For the purposes of this chapter, the term inorganic constituents will be used to describe all ash-forming constituents including both organically associated inorganic species and mineral grains. In addition, for further clarification--*coal does not contain ash--it contains organic and inorganic components*. The inorganic part of the coal is transformed into ash during combustion.

4.2.1 Association, Size, Density, and Composition

The inorganic elements in coal occur as discrete minerals, amorphous phases, organically associated cations, and cations dissolved in pore water. The fraction of inorganic components that are organically associated varies with coal rank. Lower-ranked subbituminous and lignitic coals have high levels of oxygen. Approximately 25% of the oxygen is in the form of a carboxylic acid group. These groups act as bonding sites for cations such as sodium, magnesium, calcium, potassium, strontium, and barium (other minor and trace elements may also be associated in the coal in this form). In addition, some elements may be in the form of chelate coordination complexes with pairs of adjacent organic oxygen functional groups. The cations originate from the plant material from which the coal was formed and from groundwater filtering through the coal seam. In some low-rank coals, the organically associated inorganic components can comprise up to 60% of the total inorganic content of the coal (ref. 2). In higher-ranked coals, bituminous and anthracite, the inorganic components consist mainly of minerals.

Mineral grains are usually the most abundant inorganic component in coals. The minerals associated with coals are classified by coal geologists based on their origins as summarized by Stach *et al*. (ref. 14). The major mineral groups found in coals include silicates and oxides, carbonates, sulfides, sulfates, and phosphates. Minerals that are transported by wind and water during the first stage of coalification are called detrital minerals. The detrital minerals consist mainly of silicates including clay minerals and quartz. The detrital mineral group is usually the most abundant. Minerals that form during the initial stages of coalification or deposition of the coal bed are called syngenetic. These minerals include carbonates, sulfides, some oxides, and phosphates. Minerals that form during the second stage of coalification are called epigenetic. The epigenetic minerals consisting mainly of carbonates, sulfides, and oxides that form in fissures, cleats, and cavities within the coal organic matrix. The primary difference between the epigenetic and syngenetic minerals is that the epigenetic minerals form in place in a manner which makes them more likely to be intimately mixed with the organic coal materials.

In order to predict the behavior of the inorganic constituents during combustion, detailed information must be obtained on the abundance, size, and association of mineral grains in the coal. In addition, the association of the mineral grain with the coal matrix must be determined and classified. A mineral associated with the organic part of a coal particle is said to be *included*. A mineral that is not associated with organic material is referred to as *excluded*. An additional term that has been used to describe the association of minerals is juxtaposition (ref. 15). Juxtaposition refers to the general association of minerals to coal and to other minerals. For example, a single coal particle may contain several minerals such as quartz, kaolinite, and pyrite. Figure 4.1 illustrates the type of information needed to model the chemical composition and size evolution of ash during coal combustion.

4.2.2 Methods of Determining Inorganic Associations

The methods used to determine the association of inorganic components in coals have evolved significantly over the past 80 years. Standard methods typically involve concentration of inorganic components for chemical analysis by ashing or gravity separation techniques. These methods have inherent limitations and do not provide quantitative information on the association and abundance of inorganic components in coals. Recently, more advanced methods such as computer-controlled scanning electron microscopy (CCSEM) and chemical fractionation are being used to more quantitatively determine the abundance, size, and association of inorganic components in coals.

Detailed information from the CCSEM and chemical fractionation allows for more effective prediction of the behavior of the inorganic components during combustion.
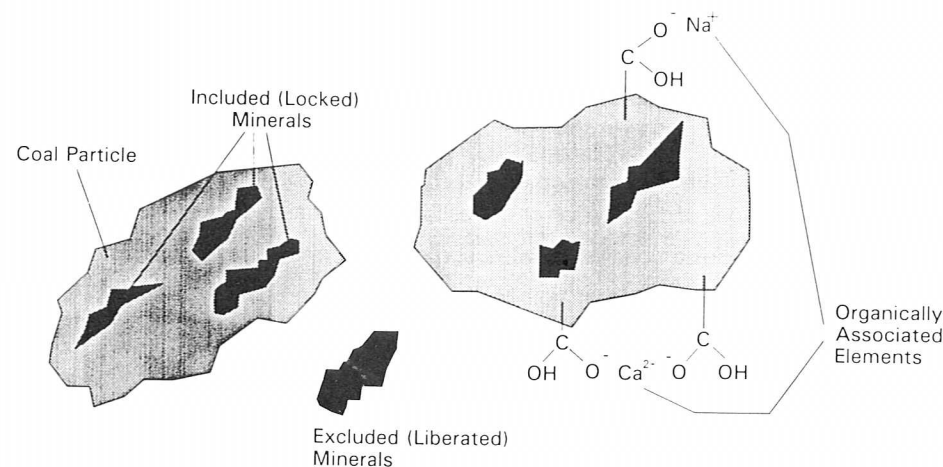

Fig. 4.1 Coal and associated inorganic components.

High-temperature ashing is a standard method that is routinely used to determine the quantity of inorganic constituents present in coal. This technique involves oxidizing the coal at 1023 K (750°C) followed by chemical analysis of the resultant ash. There are several limitations involved in this type of analysis. First, significant transformations and reactions of the inorganic components occur during the ashing process. The loss of mass due to water loss from clay minerals, carbon dioxide loss from carbonates, and sulfur loss from pyrite can significantly influence the determination of the inorganic content of coal. These species (H_2O, CO_2, and SO_2) are usually included as volatiles in the proximate analysis, leading to erroneous results. In addition, the organically associated inorganic elements such as the alkali and alkaline earth elements absorb oxygen and SO_2 during the ashing processes, further complicating the determinations. Several investigators have developed empirical methods based on the composition of the ash and losses due to decomposition of minerals to estimate the inorganic content of coals as summarized by Given and Yarzab (ref. 16).

Two other methods that have been used to concentrate the inorganic components in coal include gravity fractionation and low-temperature oxygen plasma ashing (LTA). Gravity separation only provides a partial separation of the minerals from the coal matrix, since some of the minerals that are small and included in the coal particles remain in the lighter fraction. In addition, the organically associated cations remain in the lighter

organic-rich fraction. Therefore, gravity fractionation of the minerals is only a qualitative estimation of the minerals present in the coal. Low-temperature ashing is another technique that has been used to concentrate the inorganic species. This technique works quite well with higher-rank coal, but requires very long ashing times with lower-ranked coals containing high levels of organically associated cations. The LTA technique also transforms some of the minerals that are present in the coal and produces some minerals during the processing (refs. 17, 18). Still, the LTA provides a better method to concentrate the inorganic species than either gravity separation and high-temperature ashing. The procedure, however, must be performed carefully and should probably be limited to high-rank coals.

Identification of the specific mineral species in coals (as opposed to chemical analysis) has been performed by several techniques. Jenkins and Walker (ref. 19) provide a good summary of the techniques and applications prior to 1978. These include x-ray diffraction, infrared spectroscopy, differential thermal analysis, scanning electron microscopy and microprobe analysis, and [57]Fe Mössbauer. Unfortunately, the x-ray diffraction and infrared spectroscopy methods require low-temperature ashing prior to analysis. The technique that shows the most promise for quantitative determination of the mineral portion of the inorganic components in coal is scanning electron microscopy and microprobe (energy dispersive x-ray analysis) analysis. Over the past ten years, this technique has been used much more rigorously to determine the mineral component in coal.

In order to determine the size, abundance, and association of mineral grains in both high- and low-rank coals, computer-controlled scanning electron microscopy (CCSEM) and automated image analysis (AIA) is the preferred technique used to analyze polished cross sections of coal epoxy plugs (ref. 20). The CCSEM technique is used to determine the size, shape, quantity, and semi-quantitative composition of mineral grains in coals (refs. 21, 22). The key components of the CCSEM system that make it possible to image, size, and analyze inorganic particles are the backscatter electron detector, digital beam control, and the ultrathin window energy-dispersive x-ray detector. Backscatter electron imaging is used for CCSEM because the intensity of the backscattered electrons is a function of the average atomic number of the features on or near the surface. Since the mineral particles appear brighter relative to the lower atomic number background of the matrix, a distinction can be made between coal, mounting media, and mineral grains. 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 an energy-dispersive spectrum (EDS) at that point for 2 seconds. Software classifies the mineral grains based on the EDS elemental composition and size. The parameters used to identify the minerals are based on published compositions of known minerals. A mineral association, such as aluminosilicate/gypsum, is a discrete particle that contains at least two adjacent or intimately associated minerals. The EDS spectra will reveal a combination of the proper elemental ratios for these associated minerals.

Quantification of the type and abundance of organically associated inorganic elements in lower-ranked subbituminous and lignitic coals is currently performed by chemical fractionation (ref. 2). Chemical fractionation is used to selectively extract elements from the coal based on solubility, which reflects their association in the coal. Briefly, the technique involves extracting the coal with water to remove water-soluble elements such as Na in sodium sulfate or those elements that were most likely associated with the groundwater in the coal. This is followed by extraction with 1M ammonium acetate to remove elements such as Na, Ca, and Mg that may be bound as salts of organic acids. The residue of the ammonium acetate extraction is then extracted with 1M HCl to remove acid-soluble species such as Fe and Ca which may be in the form of hydroxides, oxides, carbonates, and organically coordinated species. The components remaining in the residue after all three extractions are assumed to be associated with the insoluble mineral species such as clays, quartz, and pyrite.

4.2.3 Distribution of Inorganic Constituents in Selected Coals

Four low-ranked coals from the Argonne National Laboratory (ANL) premium coal suite were analyzed by chemical fractionation to determine the leaching behavior of Na, Mg, Al, Si, K, Ca, and Fe, with results given in Table 4.1. Those elements removed by water are loosely associated with the carbonaceous matrix; those removed by ammonium acetate are usually in the form of salts of carboxylic acid groups; and those removed by hydrochloric acid are acid-soluble mineral grains such as carbonates, oxides, hydroxides, sulfates, and organically coordinated inorganic elements. The elements remaining are associated with the insoluble mineral species. Most of the sodium and magnesium and much of the calcium and potassium were removed by the water and ammonium acetate extractions, indicating an organic carboxylate association for these elements. Aluminum and silicon generally remain with the insoluble mineral species. Much of the iron, especially in the Dietz coal, is removed by HCl, indicating that iron is found predominantly

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.

as carbonates, oxides, hydroxides, sulfates, and organically coordinated inorganic elements for these low-rank coals. For the Beulah-Zap lignite, most of the Ca, Na, Mg, and K are bound to carboxyl groups or possibly on ion-exchange sites with clays (ref. 2) and consequently has a higher fouling potential than the other coals (ref. 23). The association of other species as oxides, carbonate minerals, and coordinated metal ions can also be seen from the extractions by HCl.

The complete quantitative CCSEM results for the eleven selected research coals (see Chapter 2) are presented in 33 tables in Zygarlicke et al. (ref. 24). A summary of these results is given in Table 4.2. As expected, the pyrite content in the Illinois #6 coal is high. The excluded content of specific minerals and mineral associations are summarized in Table 4.3. This analysis is performed on a bulk basis, and results are in frequency percentage. For example, 42% of the quartz in the Upper Freeport coal is excluded (i.e., 42% of the quartz was observed outside of the coal particles), and, accordingly, 58% of the quartz in the coal is included or observed within coal particles. Only a fraction of the associated mineral compositions contained in coal, such as gypsum/quartz, gypsum/aluminosilicate, quartz/rutile, or quartz/calcite, are shown in Table 4.2 since most of the mineral associations are only a minor component of the overall mineral matter. The role of morphology of the mineral grains in the interpretation of CCSEM data is discussed in Jones et al. (ref. 15).

The Upper Freeport, Illinois #6, and Pittsburgh coals were analyzed by scanning electron microscopy based upon automated image analysis for mineral composition, particle size, and association of the minerals with the organic matrix in Straszheim and Markuszewski (ref. 26) who obtained results similar to those reported by Zygarlicke et al. (ref. 24) and in Tables 4.2 and 4.3. These results were used to predict cleanability or the anticipated coal recovery versus mineral rejection for density- and surface-based cleaning processes.

The differences in the chemical information provided by the ASTM versus more advanced methods such as CCSEM are illustrated in Fig. 4.2. The ASTM analysis (Fig. 4.2a) provides only a single data point which does not represent the true heterogeneity of the ash, in contrast to the CCSEM analysis of the ash (Fig. 4.2b).

4.3 FORMATION OF ASH INTERMEDIATES

The inorganic coal components undergo complex chemical and physical transformations during combustion to produce intermediate ash species which consist of gases, liquids, and solids. The partitioning of the inorganic components during

TABLE 4.2

Quantitative Mineral Content Data for the Eleven Research Coals by CCSEM Analysis (ref. 25)[a]

Mineral	Upper Freeport (MVB) Total wt% (minerals)	Total wt% (coal)	Wyodak (SubC) Total wt% (minerals)	Total wt% (coal)	Illinois #6 (HVCB) Total wt% (minerals)	Total wt% (coal)	Pittsburgh (HVAB) Total wt% (minerals)	Total wt% (coal)	Pocahontas #3 (LVB) Total wt% (minerals)	Total wt% (coal)	Blind Canyon (HVBB) Total wt% (minerals)	Total wt% (coal)
Quartz	15.65	2.24	14.13	0.94	10.91	1.91	14.74	1.50	7.86	0.43	14.91	0.91
Iron Oxide	1.52	0.22	1.55	0.10	0.30	0.05	0.67	0.07	22.57	1.22	4.03	0.25
Aluminosilicate	12.05	1.72	15.92	1.05	9.03	1.58	25.42	2.59	16.81	0.91	22.45	1.37
Ca-Aluminosilicate	0.22	0.03	3.41	0.23	0.04	0.01	0.22	0.02	0.40	0.02	0.29	0.02
Fe-Aluminosilicate	2.36	0.34	0.95	0.06	2.61	0.46	1.24	0.13	11.52	0.62	1.34	0.08
K-Aluminosilicate	31.79	4.54	17.92	1.19	17.21	3.01	25.01	2.55	5.46	0.29	16.50	1.01
Ankerite	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.01	1.39	0.08	0.78	0.05
Pyrite	29.15	4.17	37.54	2.49	40.18	7.02	25.53	2.60	7.12	0.39	14.41	0.88
Gypsum	0.68	0.10	0.34	0.02	9.56	1.67	0.26	0.03	0.56	0.03	3.16	0.19
Barite	0.00	0.00	0.10	0.01	0.00	0.00	0.00	0.00	0.07	0.00	0.23	0.01
Gypsum/Barite	0.00	0.00	1.10	0.07	0.00	0.00	0.00	0.00	0.09	0.01	0.00	0.00
Apatite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.02	0.00	0.00
Ca-Silicate	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.81	0.04	0.20	0.01
Alumina	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.29	0.34	0.18	0.01
Aluminosil./Gypsum	0.16	0.02	0.59	0.04	0.15	0.03	0.09	0.01	0.03	0.00	0.17	0.01
Ca-Aluminate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Calcite	2.98	0.43	0.31	0.02	5.29	0.93	0.82	0.08	12.21	0.66	7.76	0.47
Rutile	0.33	0.05	1.01	0.07	0.17	0.03	0.59	0.08	0.59	0.03	0.07	0.00
Dolomite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.21	0.01
Ca-Rich	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.01	0.12	0.01	1.22	0.07
Si-Rich	0.17	0.02	1.05	0.07	0.48	0.08	0.39	0.04	2.70	0.15	5.87	0.36
Periclase	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.01
Unknown	2.96	0.42	4.00	0.26	4.08	0.71	5.49	0.56	3.09	0.17	6.14	0.37

[a]The mineral content is further given in a particle-size distribution in Zygarlicke et al. (ref. 25). Total wt% (minerals) = weight % on a mineral basis. Total wt% (coal) = weight % on a coal basis. Quartz = SiO_2; Al-Silicate (Kaolinite) = $Al_4Si_4O_{10}(OH)_8$; Fe-Aluminosilicate = Fe_xAl_y, Si_z; K-Aluminosilicate (Illite) = $K(Al, Fe)_4(Si, Al)_8O_{20}(OH)_4$; Ca-Aluminosilicate = Ca_xAl_y, S_z; Iron Oxide = Fe_2O_3; Pyrite = FeS_2; Gypsum = $CaSO_4 \cdot 2H_2O$; Calcite = $CaCO_3$; Rutile = TiO_2; Barite = $BaSO_4$; Ankerite = $Ca(Mg, Fe, Mn)(CO_3)_2$; Siderite = $FeCO_3$; Crandallite = $CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$, Dolomite = $CaMg(CO_3)_2$; Calcium Aluminate = $Ca_3Al_2O_6$; Apatite = $Ca_5F(PO_4)_3$; Spinel = $(Fe, Al, Mg)O_4$; Calcium Silicate = $CaSIO_3$; and Pyrrhotite/Iron Sulfate = FeS.

TABLE 4.2 (continued)

Quantitative Mineral Content Data for the Eleven Research Coals by CCSEM Analysis (ref. 25)[a]

Mineral[a]	Lewiston-Stockton (MVB)		Beulah-Zap[b] (LigA)		Lower Wilcox (LigA)		Dietz (SubB)		Buck Mountain (AN)	
	Total wt% (minerals)	Total wt% (coal)	Total wt% (minerals)	Total wt% (coal)	Total wt% (minerals)	Total wt% (coal)	Total wt% (minerals)	Total wt% (coal)	Total wt% (minerals)	Total wt% (coal)
Quartz	24.87	2.87	18.00	1.00	37.63	2.59	15.39	0.57	0.29	0.01
Iron Oxide	0.55	0.06	1.36	0.08	0.00	0.00	2.86	0.11	1.46	0.06
Aluminosilicate	44.13	5.12	41.72	2.33	14.39	0.99	39.85	1.47	31.91	1.37
Ca-Aluminosilicate	0.22	0.03	0.17	0.01	19.61	1.35	1.70	0.06	2.64	0.11
Fe-Aluminosilicate	0.89	0.10	0.28	0.02	7.38	0.51	0.00	0.00	20.67	0.88
K-Aluminosilicate	23.42	2.72	0.79	0.04	7.58	0.52	7.95	0.29	27.02	1.16
Ankerite	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.02	0.00
Pyrite	0.93	0.11	25.65	1.43	0.18	0.01	13.93	0.51	5.04	0.22
Gypsum	0.00	0.00	2.13	0.12	0.00	0.00	3.90	0.14	0.04	0.00
Barite	0.05	0.01	1.58	0.09	0.21	0.02	5.52	0.20	0.00	0.00
Gypsum/Barite	0.00	0.00	0.26	0.01	0.07	0.01	0.10	0.00	0.00	0.00
Apatite	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca-Silicate	0.52	0.06	0.43	0.02	0.13	0.01	0.08	0.00	0.00	0.00
Alumina	0.09	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.35	0.02
Aluminosil./Gypsum	0.00	0.00	0.00	0.00	0.88	0.06	0.01	0.00	0.00	0.00
Ca-Aluminate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Calcite	0.03	0.00	0.08	0.01	1.23	0.09	1.01	0.04	0.56	0.02
Rutile	0.39	0.05	0.29	0.02	1.77	0.12	0.32	0.01	0.00	0.00
Dolomite	0.02	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.20	0.00
Ca-Rich	0.10	0.01	0.03	0.00	0.00	0.00	0.04	0.00	0.25	0.01
Si-Rich	0.32	0.04	0.31	0.02	3.54	0.24	0.93	0.03	0.00	0.01
Periclase	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Unknown	3.49	0.40	6.83	0.38	5.40	0.37	6.43	0.24	7.86	0.34

[a]The mineral content is further given in a particle-size distribution in Zygarlicke et al. (ref. 25). Total wt% (coal) = weight % on a coal basis. Total wt% (minerals) = weight % on a mineral basis. Quartz = SiO_2; Al-Silicate (Kaolinite) = $Al_4Si_4O_{10}(OH)_8$; Fe-Aluminosilicate = $Fe_xAl_y Si_z$; K-Aluminosilicate (Illite) = $K(Al,Fe)_4(Si,Al)_8O_{20}(OH)_4$, Ca-Aluminosilicate = Ca,Al,Si_x, Iron Oxide = Fe_2O_3; Pyrite = FeS_2; Gypsum = $CaSO_4 \cdot 2H_2O$; Calcite = $CaCO_3$; Rutile = TiO_2; Barite = $BaSO_4$; Ankerite = $Ca(Mg,Fe,Mn)(CO_3)_2$; Siderite = $FeCO_3$; Crandallite = $CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$; Dolomite = $CaMg(CO_3)_2$; Calcium Aluminate = $Ca_3Al_2O_6$; Apatite = $Ca_5F(PO_4)_3$; Spinel = $(Fe,Al,Mg)O_4$; Calcium silicate = $CaSiO_3$; Pyrrhotite/Iron Sulfate = FeS.

[b]PSI/DOE Beulah lignite.

TABLE 4.3

Excluded Content of Minerals and Mineral Associations for the Eleven Research Coals by CCSEM Analysis (%) (ref. 25)

Mineral Types[a]	Upper Freeport	Wyodak	Illinois #6	Pittsburgh	Pocahontas #3	Blind Canyon	Lewiston-Stockton	Beulah-Zap	Lower Wilcox	Dietz	Buck Mountain
Quartz	42	37	47	52	50	65	59	51	24	66	100
Aluminosilicate	52	52	57	46	49	68	71	31	32	63	65
Fe-Aluminosilicate	52	38	50	30	32	33	67	44	29	62	57
K-Aluminosilicate	42	16	46	43	53	73	76	0	30	56	88
Ca-Aluminosilicate	0	33	33	50	25	80	0	33	12	20	75
Iron Oxide/Siderite	33	—	—	—	38	57	—	20	—	—	—
Iron Oxide	—	—	—	—	—	—	100	—	—	67	100
Pyrite	47	41	51	58	48	70	—	36	0	62	100
Calcite	33	33	68	20	53	68	100	0	100	100	50
Rutile	100	33	—	—	75	—	67	67	33	—	—
Apatite	—	15	—	—	—	0	—	—	—	—	—
Ankerite	—	—	—	—	50	44	—	—	0	50	100
Barite	—	0	100	—	—	33	100	50	—	—	—
Dolomite	—	—	—	—	—	100	—	—	6	65	—
Gypsum	33	67	46	50	33	63	100	33	0	0	100
Gypsum/Aluminosilicate	—	9	20	40	100	40	100	20	—	—	—
Gypsum/Barite	—	0	—	—	—	—	—	25	0	100	100
Gypsum/Quartz	—	0	25	50	—	0	—	50	—	—	—
Gypsum/Barite/K-Alumino.	—	—	—	—	—	—	—	—	—	—	—
Gypsum/Barite/Alumino.	—	—	—	—	—	—	—	100	—	—	50
Aluminosilicate/Apatite	75	0	—	—	25	—	100	—	—	50	—
Aluminosilicate/Barite	—	—	—	—	—	—	—	—	—	—	63
Aluminosilicate/Calcite	25	—	43	50	—	—	—	—	—	100	—
Aluminosilicate/Pyrite	—	—	—	—	100	100	—	—	—	0	—
Aluminosilicate/Rutile	100	100	—	—	—	—	—	—	—	—	—
Ca-Aluminosilicate/Gypsum	—	—	—	—	—	—	—	—	0	—	—
Ca-Alumino./Gyp./Barite	—	—	—	75	—	—	—	100	—	—	—
K-Aluminosilicate/Pyrite	90	—	—	—	—	100	100	—	—	—	—
Quartz/Barite	67	—	100	44	—	—	—	67	—	—	0
Quartz/Calcite	—	—	—	50	67	100	—	—	33	—	—
Quartz/Pyrite	40	0	38	—	0	—	0	—	—	—	—
Quartz/Rutile	20	0	—	—	100	—	—	—	—	—	—
Quartz/Siderite	100	—	—	—	—	—	—	33	—	—	—
Quartz/Gypsum/Barite	—	—	—	—	—	—	—	—	—	—	—
Quartz/Pyrite/Gypsum	—	—	—	—	—	—	—	100	—	—	—
Pyrite/Barite	—	—	—	—	—	—	—	—	—	—	—
Calcium Silicate	—	—	—	—	80	—	—	—	—	—	100
Silica-Rich	—	—	—	—	—	—	100	—	—	50	100
Alumina	—	—	—	—	—	—	—	—	—	—	0
Pyrrhotite/Fe-Sulfate	—	—	—	—	—	—	—	—	—	—	100
Apatite/Crandallite	—	—	—	—	—	—	—	—	—	—	—
Unknown	75	20	50	33	33	67	0	—	80	56	56

[a]Excluded % = wt% in excluded category. Excluded minerals are not associated with carbonaceous material. Included minerals are associated with or contained within a carbonaceous coal particle. Included % = 100 (% Excluded). Most mineral associations are only a minor component of mineral matter and are not included in Table 4.2.
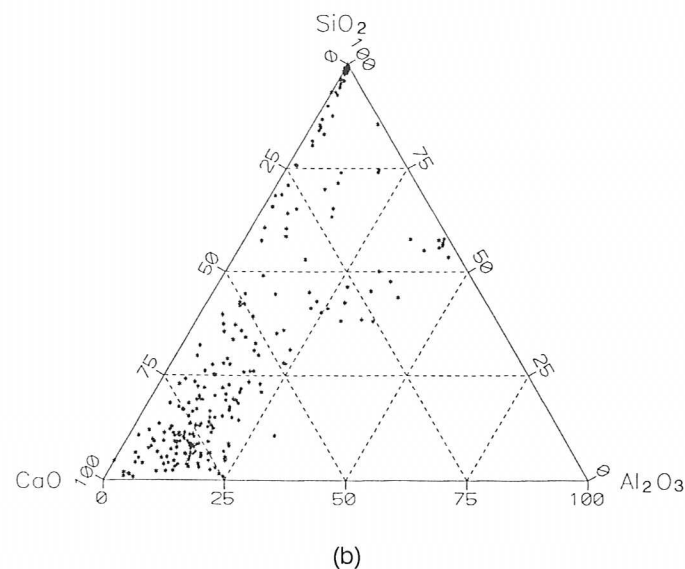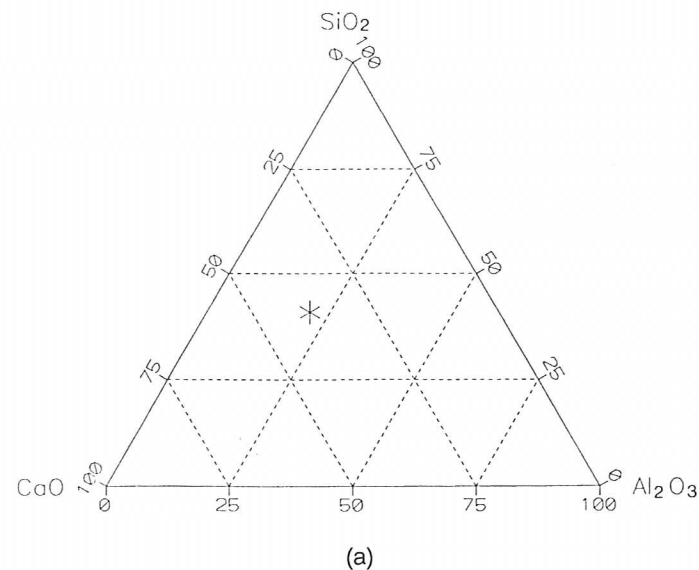
(a)

(b)

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.

combustion to form ash intermediates depends upon the association and chemical characteristics of the inorganic components, the physical characteristics of the coal particles, the physical characteristics of the coal minerals, and the combustion conditions. In order to predict the effects of inorganic constituents on combustion systems, the mechanisms by which the size and composition of intermediate ash species are formed must be elucidated. The size and composition of the intermediate ash species directly influence slagging and fouling problems in combustion systems.

4.3.1 Physical Transformations of Inorganic Constituents

The physical transformation of inorganic constituents depends on the inorganic composition of the coal and combustion conditions. The inorganic components illustrated in Fig. 4.1 can consist of organically associated cations, mineral grains that are included in coal particles, and excluded mineral grains. There is a wide range of combinations of mineral-mineral, mineral-coal, mineral-cation-coal, and mineral-mineral-cation-coal associations in coal. These associations are unique to each coal sample. Figure 4.3 illustrates the types of transformations that are likely to occur during the coal combustion process.

The physical transformations involved in fly ash formation illustrated in Fig. 4.3 include (1) coalescence of individual mineral grains within a char particle, (2) shedding of the ash particles from the surface of the chars, (3) incomplete coalescence due to disintegration of the char, (4) convective transport of ash from the char surface during devolatilization, (5) fragmentation of the inorganic mineral particles, (6) formation of cenospheres, and (7) vaporization and subsequent condensation of the inorganic components upon gas cooling. As a result of these interactions, the resulting ash has a bimodal size distribution as illustrated in Fig. 4.4. The submicron component is largely a result of the condensation of flame-volatilized inorganic components. The mass mean diameter of the larger particles is approximately 12 to 15 micrometers, depending upon the coal and the combustion conditions. The larger size particles have been called the residual ash by some investigators (ref. 3) because these ash particles resemble, to a limited degree, the original minerals in the coal.

The transformations of excluded minerals are dependent upon the physical characteristics of the mineral. Excluded minerals such as quartz (SiO_2) can be carried through the combustion system with its angular structure still intact. Excluded clay minerals can fragment during dehydration, melt, and form cenospheres. The behavior of excluded pyrite depends upon its morphology. Some of the pyrite may be present as
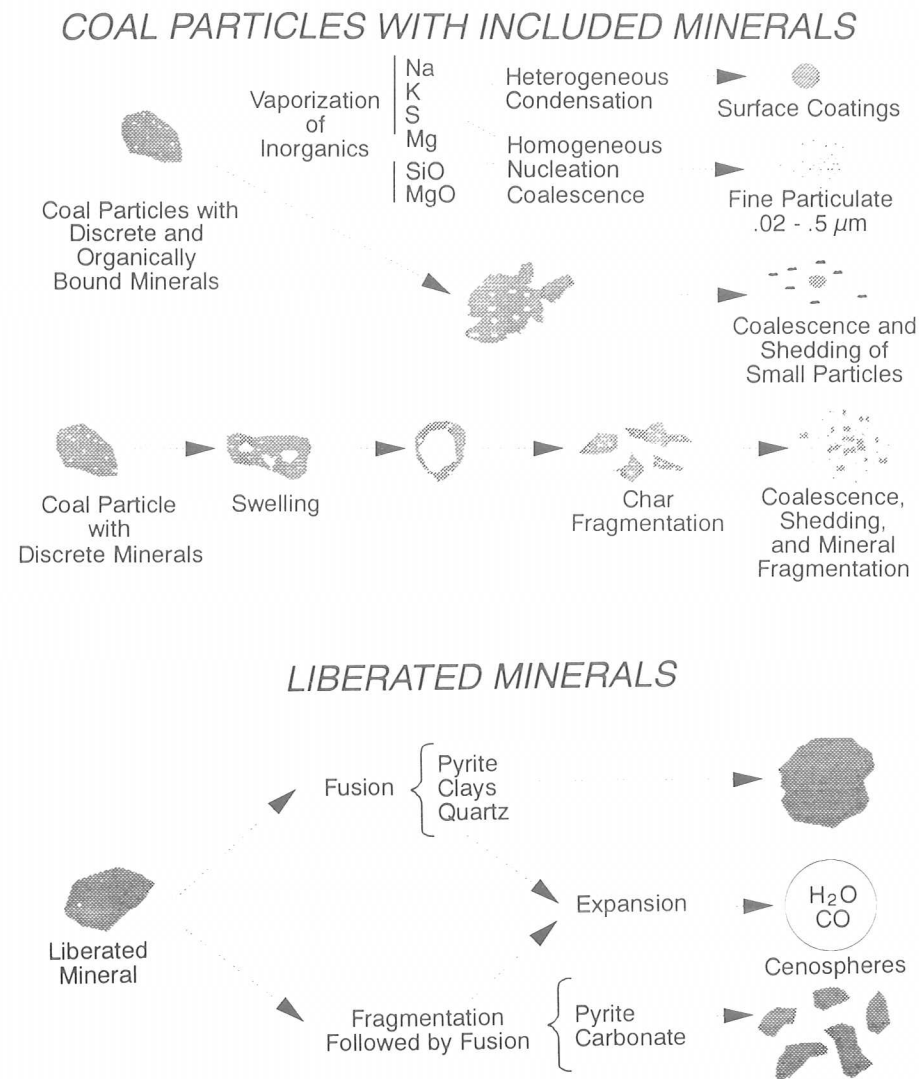
COAL PARTICLES WITH INCLUDED MINERALS

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

LIBERATED MINERALS

Liberated Mineral

Fusion { Pyrite Clays Quartz ▶

Expansion ▶ H$_2$O CO Cenospheres

Fragmentation Followed by Fusion { Pyrite Carbonate ▶

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

framboids. Framboidal pyrite fragments more easily than massive pyrite particles. In addition, pyrite transforms to pyrrhotite and oxidizes to FeO, Fe$_3$O$_4$, and Fe$_2$O$_3$ during combustion. The transformations of pyrite have been examined and modeled in detail by Srinivasachar et al. (ref. 27). The carbonate minerals will fragment during the loss of

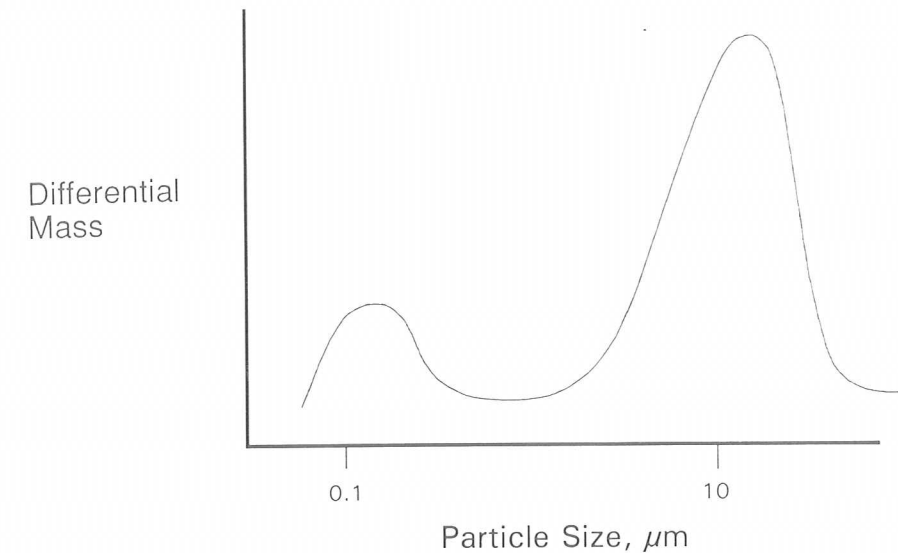Differential Mass

0.1   10

Particle Size, μm

Fig. 4.4 Size distribution of fly ash produced during combustion.

carbon dioxide. According to Raask (ref. 6), some of the carbonate minerals fragment and produce submicron-sized particles.

The transformations of the included mineral grains are dependent upon the combustion characteristics of the char particle. Coal combustion may be considered as a two-stage process consisting of devolatilization and char combustion. The first stage involves the heat-up and pyrolysis of the coal particles and includes the release, ignition, and combustion of the volatiles. The second stage is the oxidation of the char. The stages often occur sequentially, but they can occur simultaneously. The devolatilization stage is rapid compared to the char combustion. The overall process of coal particle combustion takes less than one second for typical pulverized coal particles. The combustion gases may reach temperatures as high as 1810 K, but the temperature of the burning char particle may be up to 200-400 K higher. The temperature depends upon the percent excess air, quality of coal, fuel-air mixing, and coal particle size. During combustion, most of the nonvolatile inorganic species remain with the char. A very small amount of ash is found associated with the volatiles (ref. 3).

There are two extreme behaviors that the inorganic constituents may exhibit during combustion (ref. 28). In one extreme, each mineral grain forms a single ash particle. In the other, one ash particle is formed per coal particle. Some of the differences in the fly ash size distributions exhibited for different coals are probably due to the burning char characteristics of the chars. For example, some coal particles swell and become hollow and porous during combustion. The degree of swelling depends on coal composition or maceral distribution and the combustion conditions. A highly vesicular char particle burns on several expanding combustion fronts, causing disintegration of the char particle into smaller particles. Most ash particles associated with the char have a sufficiently high surface tension that they do not wet the surface of the char particles. Depending upon the distribution of minerals and other inorganic components, there may be little or no coalescence. Therefore, the ash particles may be similar in size to the original minerals in the coal, producing one ash particle per mineral grain. In contrast, coalescence of minerals into a larger particle occurs when the receding carbon surface brings the ash particles together. Therefore, coalescence is important for nonswelling coal particles that tend to burn as shrinking spheres. A shrinking sphere represents the limiting case where one fly ash particle is produced per coal particle. In most cases, the actual fly ash size falls between the fine limit of one ash particle per mineral grain and the coarse limit of one ash particle per coal particle. In cases where mineral fragmentation occurs, the fine limit on size may be exceeded. In addition, shedding or convective transport of small ash particles originating from organic associations or submicron mineral grains can also contribute to fine particle formation.

Vaporization and condensation of inorganic elements contribute to the formation of fine particulate when the vapors condense homogeneously. In addition, these vapors can condense on surfaces of entrained ash particles and ash deposits, producing low melting point phases. The volatility of an inorganic species depends on the coal particle temperature, the vapor pressure of the species, and the local gas phase environment. Near the surface of the particle, reducing conditions in the gas phase are expected due to the burning of the carbon material. The presence of localized reducing conditions may produce more volatile species than would occur under oxidizing conditions.

In lower-ranked lignitic and subbituminous coals, organically associated inorganic elements such as sodium, calcium, magnesium, and potassium have the potential to vaporize during combustion. The evidence for vaporization and condensation of sodium and potassium is abundant. The reactions of calcium and magnesium are less clear. During the combustion of the coal and char particle, a boundary layer at the surface of

the particle may be sufficiently low in oxygen to allow for the vaporization of calcium and magnesium. If the calcium and magnesium were to vaporize, it is likely that once they reach an environment that contains some oxygen ($\approx$3% O_2) they would rapidly oxidize, producing submicron particulates. Partially combusted char particles produced from coals containing organically associated calcium have been examined under the SEM. Small particles rich in calcium were found on the surface of the char particles (Fig. 4.5). These particles may be the result of condensed calcium species or the result of species exposed as the char surface receded. In addition, there is significant evidence that reactions occur between the organically associated cations and mineral grains associated in the coal particle during the char combustion stage.
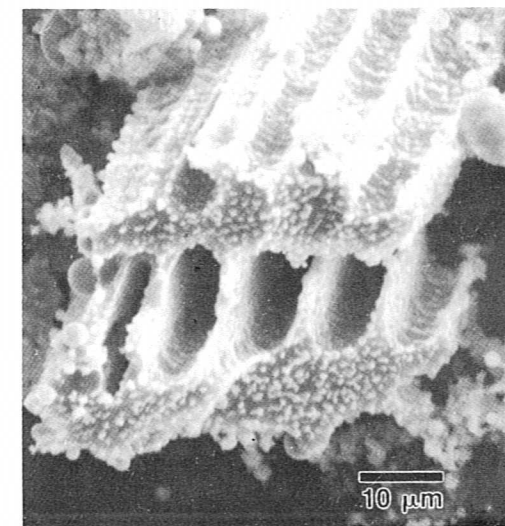

Fig. 4.5 SEM micrograph of the surface of a char produced from a coal containing high levels of organically associated calcium.

4.3.2 Chemical Transformations of Inorganic Constituents

Several chemical systems need to be considered when discussing the chemical transformations relative to the formation of ash intermediates and deposits. These include the aluminosilicate, silicate, sulfate, phosphate, chloride, and sulfide systems. In addition, iron, alkali, and alkaline earth oxides also play an important role. The dominance of one system over another is a function of residence time, excess air, and temperature. For example, the iron oxides and iron sulfides play a role in the formation of slag deposits in the radiant section of the combustor. Problems occur when the residence time,

temperature, and oxygen levels are such that they limit the oxidation of the FeS_2 to Fe_2O_3 or Fe_3O_4. If low melting point intermediate phases such as FeS and FeO form, particles rich in FeO and FeS can stick to the heat-transfer surfaces. For systems which consist primarily of silicates and sulfates, ash behavior is dominated by silicates at temperatures above 1273 K. At temperatures between ≈1170 - 1300 K both silicate and sulfate liquid phases play a role in the liquid phase formation. At temperatures below ≈1170 K, the sulfates play the primary role in deposit formation. In addition to the sulfates and silicates, the phosphate systems may also contribute to the formation of deposits.

The chemical composition of the intermediate ash particles will influence their melting behavior in combustion systems. Figure 4.6 illustrates the composition evolution of Upper Freeport fly ash. The figure shows that the major minerals such as pyrite, aluminosilicates, and K-aluminosilicates are transformed during the combustion process. The result is the formation of iron oxides, iron aluminosilicates, and other complex glass phases. These fly ash particles vary widely in size and chemical composition.

UPPER FREEPORT COAL
(Wt. % - Mineral Basis)

Quartz 12.60%
Associated Minerals* 12.26%
Iron Oxide 1.88%
Pyrite 13.76%
Aluminosilicate 24.36%
COAL
Fe-aluminosilicate 3.56%
K-aluminosilicate 31.60%

Quartz 12.10%
Amorphous Silicates 35.70%
Iron Oxide 13.90%
FLY ASH
K Aluminosilicate 18.10%
Fe Aluminosilicate 5.40%
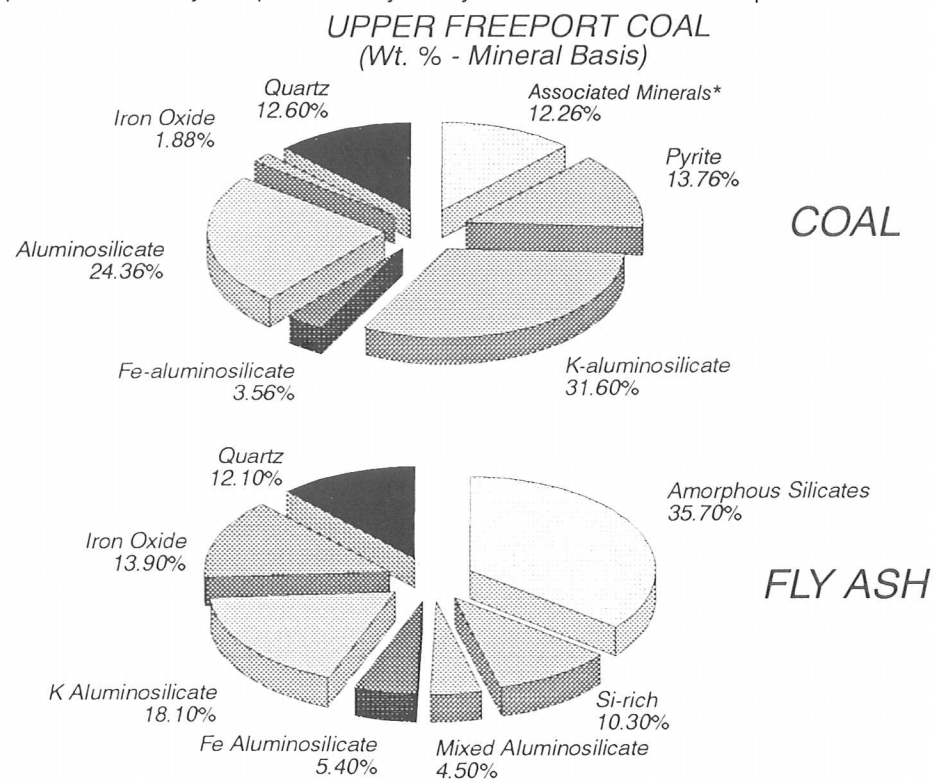Mixed Aluminosilicate 4.50%
Si-rich 10.30%

Fig. 4.6 Composition evaluation of Upper Freeport Bituminous coal ash during combustion (wt % mineral basis): (a) coal composition, (b) fly ash composition. *Mixed minerals such as quartz and pyrite.

In general, fly ash produced during pulverized coal combustion is approximately 90 to 95% amorphous and consists mainly of silicate glass. Glass is defined as an inorganic product of fusion which has cooled to a rigid condition without crystallizing. It is considered to be liquid with a very high viscosity. Understanding the behavior of the glass phases is essential in developing a means for predicting ash deposition processes. The glass/liquid material in ash intermediates is important because it influences the reactivity of the deposited ash particles and the ability of the deposit to develop strength through sintering.

The conditions for glass formation have been discussed by Kingery et al. (ref. 29). Glass-forming oxides, sometimes referred to as network formers, have the ability to build and form three-dimensional, random networks. The oxides that are good network formers include SiO_2, B_2O_3, GeO_2, P_2O_5, and AsO_4. These network formers form highly covalent bonds with the oxygen atoms. In contrast, a network-modifying oxide is incapable of building a continuous network. The addition of such a modifying oxide to a network causes weakening of the network. Good examples of network modifiers are oxides of sodium, magnesium, calcium, and potassium. Addition of a network modifier to a continuous network breaks up the network by adding oxygen to produce nonbridging oxygens. For example, the addition of Na_2O to a silicate glass causes the formation of two nonbridging oxygens, one of which was contributed by Na_2O; the sodium ion is available to balance the charge. The addition of a network modifier to a silicate glass reduces the viscosity and increases the thermal expansion coefficient. Also, some intermediate oxides are not capable of forming a glass, but can take part in the glass network. A good example of an intermediate oxide is alumina.

An element that can act as either a network modifier or an intermediate oxide is iron. In coal ash systems, the effect of iron on the silicate glasses is extremely important. The oxidation state of the iron dictates whether iron will exist as a network modifier or an intermediate. Iron present as FeO (Fe^{2+}) will act as a network modifier, resulting in the formation of nonbridging oxygens and weakening the network. Iron present as Fe_2O_3 (Fe^{3+}) will act as an intermediate oxide and may take part in the glass network.

Although glasses do not exhibit the long range order found in crystalline phases, insight into the silicate structures found in glasses can be gained by examining the silicate structural units in crystalline materials. The effect of the oxygen to silicon ratio on silicate network structures is illustrated in Fig. 4.7. The structural units observed for some of the common silicate systems are summarized in Table 4.4, and the crystalline forms and common crystalline silicate phases observed in ash deposits are shown in Table 4.5. In
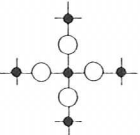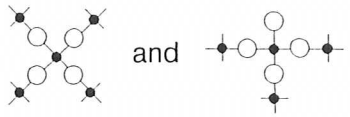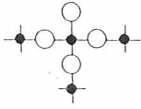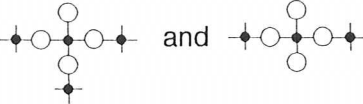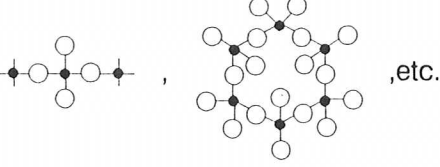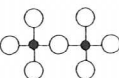
Oxygen-Silicon Ratio	Silicon-Oxygen Groups	Structure
2	Network, $(SiO_2)_{n'}$	
2-2.5	Network,	and
2.5	Network,	
2.5-3.0	Network and chains or rings,	and
3.0	Chains and rings,	, ,etc.
3.0-3.5	Chains, rings, and pyrosilicate ions	
3.5	Pyrosilicate ions,	
3.5-4.0	Pyrosilicate and orthosilicate ions	
4.0	Orthosilicate ions,	

Fig. 4.7 Effect of oxygen-silicon ratio on silicate structures (ref. 29, with permission from Wiley-Interscience).

many cases, the deposits can be analyzed by x-ray diffraction to determine the distribution of crystalline phases. The types of crystalline phases present depend upon the composition of the ash and the conditions of the system. The crystallization behavior of ashes and slags can provide insight into the time and temperature conditions to which the deposit or fly ash were subjected.

TABLE 4.4

Structural Units Observed in Crystalline Silicates

Oxygen-Silicon Ratio	Silicon-Oxygen Groups	Structural Units	Examples
2	SiO_2	3-Dimensional Network	Quartz (SiO_2)
3	SiO_3	Chain-Rings	Pyroxenes
3.5	Si_2O_7	Tetrahedra Sharing One Oxygen Ion	Pyrosilicate
4	SiO_4	Isolated Tetrahedra	Orthosilicate

TABLE 4.5

Cyrstalline Forms and Examples of Specific Cyrstal Silicate Species

Crystalline Forms	Structural Units	Examples
Orthosilicates	$(SiO_4)^{4-}$	Fayalite - Fe_2SiO_4
Pryosilicates	$(Si_2O_7)^{6-}$	Melilite (Gehlenite-Akermanite) $Ca_2Al_2SiO_7$ - $Ca_2MgSi_2O_7$
Metasilicates	$(SiO_3)_n^{2n-}$	Pyroxenes (Diopside - Augite) $CaMgSi_2O_6$ - $Ca(Fe, Mg)Si_2O_6$
Framework Silicates	Al^{3+} Replaces Si^{4+} in Tetrahedra	Plagioclase (Albite - Anorthite) $NaAlSi_3O_8$ - $CaAl_2Si_2O_8$

Liquid sulfate phases also contribute to the formation of depositions in combustion systems. These phases have very little tendency to form chains, rings, and network structures typical of silicates. The sulfate phases form as a result of the reaction of sulfur oxides with alkali and alkaline earth oxides such as sodium and calcium, respectively. The sulfur oxides form from the oxidation of sulfides and organic sulfur during combustion. These oxides can then react with ash in the combustor. It has been shown that the maximum amount of reaction between sulfur oxides and ash occurs at approximately 830 K and is dependent upon the quantity of alkali and alkaline earth

oxides in the ash (ref. 30). The exact manner in which sulfates form is not well understood. It has been postulated that sulfates form in the gas stream and condense on the surfaces of materials such as fly ash particles or boiler surfaces. However, it is more likely that sulfates are formed on particle or deposit surfaces where an alkali layer (e.g. NaOH) is first deposited, followed by the sulfur oxide interaction.

The behavior of alkali species such as sodium is extremely important with respect to the formation of convective pass fouling deposits. The mechanisms by which sodium forms deposits have been investigated by a number of researchers (refs. 23, 31). Sodium present as salts of organic acid groups in the coal will readily volatilize in a pulverized coal flame. According to Raask (ref. 6), volatile sodium can easily dissolve in the surfaces of silicate particles or become sulfated. Sodium silicate ($Na_2Si_2O_5$) was found to be thermodynamically more stable than sulfates at temperatures from 1470 - 1870 K, while sodium sulfate was stable below approximately 1370 K. In fact, the formation of Na_2SO_4 at temperatures less than approximately 1300 K inhibited the formation of sodium silicate (ref. 32). Therefore, the distribution of volatile sodium between silicate components of the ash and sulfate is influenced by temperature, as well as the residence time, of the particle in the flame. In addition, the association of the silicate mineral grains within the Na-rich organic portion of the coal will allow for the reaction of sodium to form low melting point sodium-silicates. This will limit the vaporization of the sodium during combustion. Raask suggests that, on the average, 60% of the sodium is dissolved in the silicate phase and the remaining percentage will form sodium sulfate (ref. 6). This estimate appears to be quite high for western U.S. coals having high sodium contents, but may be reasonable for coals having lower sodium contents and higher concentrations of silicate minerals.

Wibberley and Wall (ref. 33) examined the reactions involving silicon-bearing minerals and volatile sodium. Quartz subjected to high temperature gases in a vertical tube furnace was found to be relatively unaltered in the furnace. However, in the presence of alkali in the furnace gases, a low-viscosity sodium silicate phase was formed. Experiments were also performed to simulate deposit formation, using both quartz and a mixture of quartz and NaCl. The results indicated that the formation of a low-viscosity sodium silicate layer in the presence of NaCl was responsible for deposit formation. No deposit formed when using quartz alone.

Vapor pressure measurements and thermodynamic calculations (ref. 34) suggest that vapor phase sodium and potassium hydroxides or chlorides are only present in significant quantities above approximately 1200 K. Below 1200 K, the alkalies are present mainly as condensed sulfates. In addition, reactions of alkali sulfates with aluminosilicates

are thermodynamically favored over reactions with silica or quartz, and the reaction with aluminosilicates should proceed above approximately 1000 K.

4.4 DEPOSIT INITIATION

4.4.1 Ash Intermediate Species Transport

The transport of intermediate ash species is a function of the state and size of the species and system conditions such as gas flow patterns, gas velocity, and temperature. Several processes are involved as described by Raask (ref. 6) and Rosner *et al.* (ref. 35).

The primary transport mechanisms are illustrated in Fig. 4.8. The small particles (<1 μm) and vapor phase species are transported by vapor phase and small particle diffusion. These particles are characteristically rich in flame-volatilized species that condense upon cooling in the bulk gas or in the gas boundary layer next to the tube. The diffusion mechanisms that are important with respect to the transport of vapor species and small particles include:

1. Fick diffusion - molecular level.
2. Brownian diffusion - particles suspended by a host liquid.
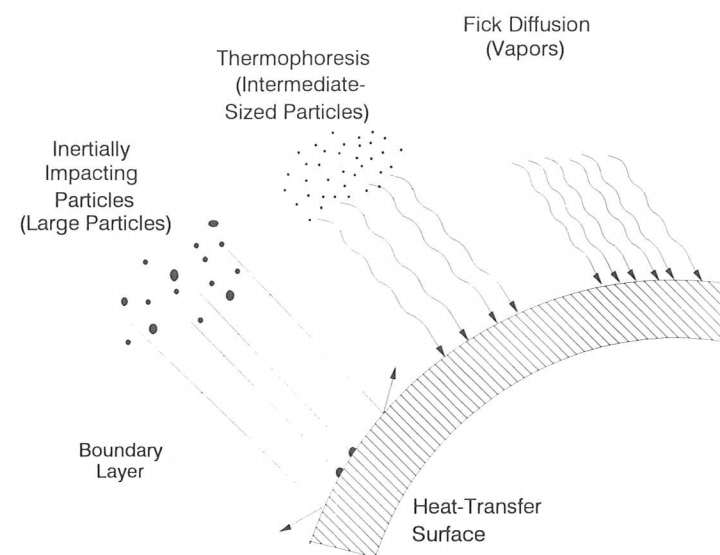3. Eddy diffusion - turbulent systems.

Fig. 4.8 Ash transport mechanisms to heat-transfer surfaces.

An additional transport mechanism which is important for the intermediate size range of particles is that of thermophoresis as illustrated in Fig. 4.8. Thermophoresis is