14
Ash-Forming Matter and Ash-Related Problems
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14.1
Analysis of Ash-Forming Matter

By proximate analysis the amount of moisture, mineral residue (ash), volatile matter, and fixed carbon is determined [1–3]. A fuel sample is crushed and dried in an oven at 105–110 °C to constant weight to determine residual moisture. The sample is then heated in a covered crucible in N₂ (to prevent oxidation) at 900 °C to constant weight. The weight loss is due to what is referred to as volatile matter. The remaining sample is then placed in an oven at 750 °C to combust the sample in air. This weight loss is attributed to fixed carbon, whereas the remaining fraction is ash (Figure 14.1). The split between volatile matter and fixed carbon will depend on the heating rate and final temperature.

In an ultimate analysis the total amount of carbon, hydrogen, nitrogen, and sulfur is determined [4, 5]. The analysis provides the main elemental composition of a fuel, usually reported on dry ash-free basis. Carbon and hydrogen are determined by combusting a sample in a closed system and analysis of the gaseous combustion products. Oxygen is usually determined by difference. Chlorine is sometimes included in the ultimate analysis as well.

Figure 14.2 shows examples of the ash content in different classes of fuels, such as coal, peat, wood-derived fuels, and agricultural residues.

Figure 14.3 shows the composition of ash-forming matter as presented in a triangular composition diagram. Here the main ash-forming matter, such as alkali metals, alkaline earth metals, and silicon are presented as oxides. The figure shows the difference between ash compositions in fuel groups. Ashes of fossil fuels and peat contain in all cases a low amount of alkali metals (<10 wt%). Forest residues are remarkably homogeneous in their composition with the exception that they may contain different amounts of sand contamination. Bark is relatively rich in calcium; in particular, eucalyptus bark contains high amounts (>70%). Agricultural residues form a group of diverse material. However, most residues contain substantial amounts of alkali metals.
Figure 14.1 Principles of standard fuel analysis.

Figure 14.2 Ash content in different fuels; coals ashed at 775 °C, biomasses ashed at 550 °C.
Besides the traditional ways described above, information on ash-forming matter can be obtained by using sequential leaching methods. Chemical fractionation is a method based on selective leaching by water, ammonium acetate, and hydrochloric acid. The method was originally developed for the characterization of coal [6]. It was modified for the characterization of biomass fuels [7] and further developed for biomass characterization and has been used for characterization of the fuels discussed in this chapter [8–13]. The method can be used to determine how ash-forming elements are bound in the fuel. Figure 14.4 give a simplified scheme, showing that the chemical fractionation technique distinguishes between the

![Figure 14.3](image1.png)

**Figure 14.3** Triangular diagram presenting the ash composition of different classes of fuels.

![Figure 14.4](image2.png)

**Figure 14.4** The chemical fractionation procedure leaches a fuel with water, ammonium acetate, and hydrochloric acid.
different types of ash-forming matter in a fuel according to their solubility in aqueous solvents. Increasingly aggressive solvents, that is, water (H_2O), 1 M ammonium acetate (NH_4Ac), and 1 M hydrochloric acid (HCl), leach samples into a series of four fractions (including the residue) for analysis. Typical ash-forming components leached out by water include alkali sulfates, carbonates, and chlorides. Elements leached out by NH_4Ac are believed to be organically associated, such as Mg, Ca, K and Na. HCl leaches the carbonates and sulfates of alkaline earth and other metals. Silicates and other minerals remain in the insoluble residue.

Figure 14.5 shows typical leaching behavior of coal. Sulfur, potassium, silicon, and aluminum are almost always non-soluble in the solvents used. Up to some 50% of iron may be dissolved at low pH in HCl or remain non-dissolved. Phosphorus may be soluble mainly at low pH. Sodium seems either present as a non-soluble silicate or water soluble. Calcium seems to be mainly organically associated.

Dissolution of Finnish peat is rather similar when compared to coal. Silicon, aluminum, potassium, and sulfur are mainly present as non-soluble matter. Almost all iron present in the fuel may dissolve at low pH. When compared to coal less magnesium is soluble at low pH. Instead Mg seems to be present mainly in an ion-exchangeable form. This also seems to be the case for calcium.

Finnish peat is rather special compared to other kinds of peat when considering the amount of iron in the fuel, which can vary from 0.5 to 5 wt%.

Solubility of ash-forming matter in wood-derived fuels is usually quite high. If the fuels are clean, that is, if no soil contamination is present almost no rest fraction will be present [14]. Figure 14.6 shows the chemical fractionation results of bark. Bark fuels are often high in calcium that has been shown to be either organically associated or calcium oxalate. Thus calcium is soluble at low pH in HCl or ion exchangeable with NH_4Ac [9].
Agricultural residues such as straws originate from fast growing species and are usually high in silicon, which plays a role in the skeleton of the fuel. Up to 5% of silicon can be soluble in water and NH$_4$Ac, that is, in a form that the plant can take up from the soil.

To study the structure of a fuel and minerals SEM analysis of samples retrieved from ashing at different temperatures such as 500, 700, and 900°C has been shown to be a valuable addition for understanding the presence of minerals in the original fuel and formed ash. Figures 14.7–14.9 show SEM pictures of
eucalyptus bark and bark ashed at 500°C, respectively. The last picture shows a close-up of the calcium oxalate crystals present [9]. These crystals are also found in other types of bark.

Ash-forming matter in a fuel consists of (Figure 14.10):

1) **Organically bound matter**: Metal ions bound to anionic organic groups in the organic molecules constituting the biomass; typically, K, Na, Mn, Ca, Mg, Fe, and Al. These are often ion exchangeable in ammonium acetate, leaching anionic
elements connected to the organic structure bound; typically, S, P, and sometimes Cl. Sulfur is often present in organic forms (covalent bonds) that are not at all, or to a limited extent only, soluble and thus remain in the insoluble part of the selective leaching procedures. Phosphorus can be present in various organic forms that may be partly soluble in acids. Chlorine may also be present in insoluble organic covalent forms (especially in waste-derived fuels containing PVC).

2) **Dissolved salts**: Metal ions and small – often inorganic – anions dissolved in plant fluids; typically, cations: K, Na, and Ca and anions Cl$^-$, HPO$_4^{2-}$, H$_2$PO$_4^-$,
SO₄²⁻, and Si(OH)₄. If the biomass is dried, these salts will precipitate, but they remain in soluble form and they will be found in the water or ammonium acetate soluble fractions of the leaching tests.

3) **Included minerals**: Minerals precipitated via natural processes in the biomass; most typically, silica (SiO₂), calcium oxalate (CaC₂O₄), and iron oxides or hydroxides (Fe(OH)₃). Silica is insoluble – even in the acidic leaching step. Precipitated calcium salts are typically insoluble in neutral aqueous solutions, but soluble in acids.

4) **Foreign matter/excluded minerals**: Soil minerals often contaminate biomasses; typically, sand and clay minerals (quartz and aluminum silicates with often some K, Na, Ca, etc.). These silicates do not dissolve in the leaching procedure and remain in the insoluble fraction. Foreign matter connected to the processing of biomass or waste, typically Fe, Al, and P, is often soluble in acid. Waste-derived foreign matter such as PVC, metallic aluminum, Pb, Zn, and Cu may have variable solubility, based on origin and form. PVC is insoluble, whereas metallic aluminum is insoluble in neutral solutions but mostly soluble in the acid leaching step. Most of the Cu and Pb is acid soluble in ionic form but practically insoluble when present in a metallic form (electronic waste). The same is true for Zn, which also may be present in ionic form or as metal.

**14.2 Release and Chemical Reactions of Ash-Forming Matter**

When a fuel is burned, the ash-forming elements that are released from the fuel undergo different reaction paths (see below for chemical reaction path for separate elements). After entering the furnace, fuel particles will heat up rapidly and dry at first. After this the pyrolysis will start, that is, organic volatile species will be released from the fuel and will burn with a visible flame. During this stage some reactive ash-forming elements will be released together with the gases. Hereafter char burning will begin. Figure 14.11 shows a scheme of the fate of ash-forming matter in coal. Most of the ash-forming elements will end up in the residual ash in the case of burning coal by the coalescence of the fused included minerals in coal during char burnout. The particle size of the residual ash depends on many factors. A single fuel particle may fragment during combustion and each fragment may produce an ash particle. The size of the ash particle will depend on the initial fuel diameter, its mineral content, the uniformity of its distribution, and the number and size of fragments produced during combustion. As reactions occur in depth within the porous char, a point is reached where the pores merge and undermine segments of the partially burned char, which are then released as fragments [15]. This description of the formation of ash is also valid for biomass fuels.

The ash size distribution at the outlet of a boiler is typically *bimodal*. Most mineral inclusions and fuel contamination are found in the large particle mode of the size distribution. The smaller particle mode represents particles of between 0.01 and
These particles are smaller than can be explained from the fragmentation of the fuel particles during conversion. The source of this fume is volatilized ash-forming matter that nucleates homogeneously as the vapors diffuse from the hot reducing atmosphere near the surface of burning char particles into the cooler oxidizing atmosphere (in the case of combustion). The nuclei are initially very small but grow rapidly by condensation of additional ash-forming vapors and by coagulation (Figure 14.12).
As stated above, when burning biomasses or wastes of various kinds the ash-forming matter is released and it reacts with the flue gas components and with each other. The fly ash formed this way becomes a complex mixture of compounds. Below follows a more detailed discussion of the fate of the most important ash-forming elements of biomass based fuels.

14.2.1 Silicon

Silicon is present as silica (SiO$_2$) or various silicate minerals. These are non-soluble in the selective leaching analysis, and will be in the rest fraction. They are relatively inert under combustion conditions. During combustion, most often the various metals connected to the silicate stay in the silicate matrix. Silicates as such are seldom a problem in fluidized beds (FB) combustion. The ash formed from them is mostly high melting and at FB conditions most silicate ashes stay in crystalline form. This kind of crystalline silicate ash does not cause slagging, fouling, sintering, or corrosion problems.

One important exception is agricultural residue such as straw, which contains high and almost equal concentrations of Si and K finely distributed in the fuel organic matrix. The major part is not chemically bound to each other and appears in different fractions of leaching tests (K is soluble, Si stays in the rest). In straw up to 25% of Si has been found soluble in water and connected to K. This is the way the plant takes up silicates (Figure 14.13).

![Figure 14.13 Solubility of Si in different fuels.](image)
During combustion these silicates easily react with each other and form low melting potassium silicates that may cause major sintering and fouling problems in fluidized beds. While being quite inert in their own behavior in combustion silica and their silicates may influence the chemistry of other ash-forming elements, especially K, Na, and Ca, by secondary reactions, thus influencing indirectly the fouling–corrosion properties of fly ash. The most important of these secondary reactions is the conversion of alkali vapors (e.g., KOH, KCl) into corresponding alkali silicates:

\[ 2 \text{KOH(g)} + \text{SiO}_2(s) \rightarrow \text{K}_2\text{SiO}_3(s, l) + \text{H}_2\text{O(g)} \]

\[ 2 \text{KCl(g)} + \text{SiO}_2(s) + \text{H}_2\text{O(g)} \rightarrow \text{K}_2\text{SiO}_3(s, l) + 2 \text{HCl(g)} \]

Besides silica, SiO\text{2}, these reactions are possible with many more complex silicates as well. The reactions have two consequences:

- they slowly modify the silicate into a lower melting alkali silicate, which may lead to bed sintering in FBs;
- they bind part of the alkali vapors, thereby changing the rest of the flue gas alkali chemistry (see K below).

14.2.2 Aluminum

Aluminum is present in many forms in biofuels and wastes. Organically bound Al or precipitated Al salts are found in the acid-soluble fractions of the leaching. In the furnace processes they all form alumina, Al\text{2}O\text{3}. This is a solid, non-reactive compound that does not significantly participate in the ash chemistry of fluidized bed systems.

In some biomass fuels Al may be present as silicates. This is the case when for instance clay or other impurities have contaminated the fuel. In the leaching tests this part of aluminum stays in the insoluble rest. In some cases such aluminum silicates are used as bed materials. Aluminum silicates are not very reactive but they may react with alkali vapors, thus influencing the flue gas alkali chemistry (see Si above and K and Cl below).

Metallic aluminum, Al(s), may be present in certain waste-derived fuels. This will be partly in the acid-soluble fraction, and perhaps partly in the rest fraction as well, depending on the source of the aluminum when using the above-described leaching tests (Figure 14.14). In combustion the metallic aluminum will have the tendency to oxidize to alumina, Al\text{2}O\text{3}(s). However, for typical aluminum residues in packaging waste derived fuels this reaction does not proceed to completion. The reaction is retarded by the formation of an Al\text{2}O\text{3} layer on the surface of the metallic aluminum. Consequently, large amounts of metallic Al will be present in the ash. Metallic Al has a low melting point (around 600 °C) and it will easily form agglomerates and deposits on tube surfaces in the furnace or superheaters.
In some wastes (sludges) aluminum may be present as an added process chemical, for example, aluminum sulfate. This will be acid soluble in the leaching tests. In combustion it will decompose and form the relatively inert Al₂O₃.

14.2.3 Iron

Iron is present in various forms in the biomass fuels. It is especially abundant in Finnish peat, where its concentration may exceed several percent of the fuel dry solids. It is also a common ingredient in sludges from water treatment processes.

Iron may be partly dissolved in the aqueous phase in the fuel, partly organically bound (Fe²⁺) and partly as a precipitated hydroxide. These are soluble in the ammonium acetate leaching or acid leaching, respectively (Figure 14.15). During combustion, all these forms of iron will yield iron oxides – FeO, Fe₃O₄, and finally Fe₂O₃. Under strongly reducing conditions some metallic iron may also form. Iron compounds can form first deposits on furnace wall tubes in PF (pulverized fuel) boilers, where furnace gas temperatures are high [16]. It is unknown whether Fe would cause similar fireside problems at the lower temperature conditions of a fluidized bed furnace. Thus it is assumed that iron oxide may be treated as inert compounds here.

In many coals, but also in some peat qualities, Fe may be present as sulfide, FeS₂(s). This will gradually oxidize to iron oxides as well, but the intermediate steps in the
oxidation may be complex and cause slagging problems in some coal firing PF boilers.

14.2.4 Potassium and Sodium

The most important ash-forming element from a fireside problems point of view is potassium. Potassium is the root cause of bed sintering, fouling, and corrosion when using biomass based fuels.

Potassium is present in the fuel in different forms, and it is of vital interest to identify these forms. Here, the selective leaching analysis of the ash-forming matter is very useful. The insoluble part of the potassium is most often in the form of silicate contaminations of the fuel (clay etc.). This part of potassium is in a very inert form and does not take part in the lively chemistry of the more reactive forms of potassium.

In biomass based fuels K is mostly in soluble form. It can be present either in ionic form in salts in the aqueous fluids of the plant or as directly organically bound K ions (Figure 14.16). These potassium compounds will be effectively released in combustion and thus be easily available for any further reactions in the flue gases. Depending on the conditions, a significant part of these compounds may form gaseous compounds. The primary vapors of potassium are KOH(g), K(g), and KCl(g). When no chlorine is present [HCl(g) in the furnace gases] K(g) is the dominant vapor under strongly reducing conditions, and KOH(g) at more oxidative conditions. When Cl is
available, the dominant K vapor is KCl(g). These vapors undergo several further reactions in the flue gases, depending on the presence of other elements, especially sulfur. K(g) and KOH(g) will condense as carbonate particles, when no sulfur is available:

\[
2 \text{KOH}(g) + \text{CO}_2(g) \rightarrow \text{K}_2\text{CO}_3(s, l) + \text{H}_2\text{O}(g)
\]

The carbonate particles formed this way are aerosols, which melt at around 860 °C. When no sulfur is present or available, KCl(g) will condense as KCl-aerosol particles or on existing fly ash. The condensed KCl(s) will be molten at furnace temperatures (mp 770 °C). Fly ash containing KCl is very corrosive; its presence on superheater tube metal surfaces results in well-known high-temperature corrosion in boilers burning biomass fuels containing Cl. It also decreases the first melting temperature of the fly ash, thus making the ash sticky at lower temperatures.

When sulfur is present, the alkali chemistry changes dramatically. All three gaseous alkali forms above will be converted into sulfates:

\[
2 \text{KCl}(g) + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) + \text{H}_2\text{O}(g) \rightarrow \text{K}_2\text{SO}_4(s, l) + 2\text{HCl}(g)
\]

This reaction leads to a chloride-free fly ash and a significant decrease of the corrosion of the superheaters. Several techniques have been developed to promote this reaction, for instance by adding in a controlled manner sulfur-containing chemicals in the fuel or in the upper furnace.
Similar sulfation takes place also with K and KOH (in the case of chlorine-free fuels):

$$2 \text{KOH}(g) + \text{SO}_2(g) + \frac{3}{2}\text{O}_2(g) \rightarrow \text{K}_2\text{SO}_4(s, l) + \text{H}_2\text{O}(g)$$

Both reactions above act as sulfur absorbing reactions. Potassium binds SO$_2$ from the flue gases into the fly ash. In the case of a high amount of alkali metals in the fuel this leads to an observable lowering of the SO$_2$ content in the flue gases.

Sodium is also present in many biomasses. However, its concentration is typically an order of magnitude lower than that of potassium. Sodium has a very similar chemistry to potassium, and the reactions described above are valid for sodium as well (Figure 14.17).

14.2.5 Calcium and Magnesium

Calcium is the element present in the highest concentration in woody biomasses. It is partially organically bonded and thus exchangeable in the ammonium acetate leaching. It is also present as crystalline salt particles, mostly calcium oxalate – especially in biomasses having a high content of Ca, such as bark [9]. This fraction of Ca is found mainly in the acid-soluble fraction of the leaching test (Figure 14.18).

The organic calcium compounds will be converted into calcium oxide. Calcium oxide has a low vapor pressure and a high melting point. Consequently, organic calcium in biomass is released in combustion as small solid particles, CaO(s).
Calcium oxalate (several crystalline forms containing crystal water) in the biomass will also form finely divided small oxide particles under hot furnace conditions according to multi-step calcination reactions:

$$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} (s) \rightarrow \text{CaC}_2\text{O}_4 (s) \rightarrow \text{CaCO}_3 (s) \rightarrow \text{CaO} (s)$$

CaO formed from organically bound calcium or from calcium oxalate is in a quite reactive form (small particle size – few micrometers). It will participate in further reactions in the furnace and flue gases.

Calcium is also present in several silicate minerals that are part of some biomasses (peat). This calcium is insoluble in the selective leaching tests. It is also quite inert under combustion conditions and normally does not influence the rest of the flue gas chemistry.

Calcium is also added as an active additive – most often as limestone – to absorb sulfur during the combustion. The calcium oxide produced from the added limestone will naturally act in a similar way as the calcium oxide produced from the natural, soluble Ca in the biomass. However, the particle size of the oxide particles from the added limestone will be significantly larger (100–200 µm) and they react less completely in flue gases as compared to the CaO particles formed from naturally occurring Ca in biomasses.

The most important reactions of calcium include sulfation:

$$\text{CaO}(s) + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CaSO}_4(s)$$

This reaction has a great significance to the rest of the flue gas chemistry, because it removes free sulfur dioxide, SO₂, from the flue gases. Consequently, SO₂ will not
be as readily available to other competing reactions such as sulfation of alkali chlorides. At high limestone additions all sulfur will be captured as calcium sulfate, and the fly ash will contain high shares of alkali chlorides.

Recarbonation may be an important reaction in some cases of fouling:

\[
\text{CaO(s)} + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s})
\]

This reaction may cause CaO particles deposited on some surfaces in the flue gas system to sinter into hard deposits (reaction induced sintering). This occurs when the flue gas temperature decreases below some 800 °C, but the reaction becomes very slow at temperatures below some 600 °C. Consequently, this reaction is possible in between these two temperatures. Examples are known from superheater tubes, also in some cases in the cyclone exits (at low load) and also in the return leg from the cyclone.

Calcium oxide may also absorb – react with – other acidic components in the flue gases such as HF and HCl:

\[
\text{CaO(s)} + 2 \text{HF(g)} \rightarrow \text{CaF}_2(\text{s})
\]

\[
\text{CaO(s)} + 2 \text{HCl(g)} \rightarrow \text{CaCl}_2(\text{s})
\]

Both reactions take place when temperatures are below 850 °C for HF absorption and below 700–750 °C for HCl absorption (thermodynamic limitation). Recently, it has been shown that CaO also reacts with phosphorus compounds to form calcium phosphate (see below). The details of this reaction are not well known yet.

Magnesium is chemically similar to calcium (Figure 14.19). It is also present as natural element in many biomasses, but in much lower concentrations than calcium.

![Figure 14.19 Solubility of Mg in different fuels.](image-url)
The combustion chemistry of magnesium is less “lively” than that of calcium. The reactions that take place with calcium do also take place with magnesium but typically at lower temperatures, often so low that they do not really have significance in combustion systems. In most cases MgO can be treated as an inert compound in combustion. One exception is a low temperature corrosion additive containing magnesium. At low temperature conditions (below 200 °C) MgO can react, selectively, with SO₃ and thus reduce the so-called acid dew point corrosion.

14.2.6 Sulfur

Sulfur is present in biomasses as both inorganic sulfate anions and as organic sulfur (Figure 14.20). According to recent studies roughly 3/4 of the sulfur in woody biomasses is organically bound and 1/4 as soluble alkali sulfates [14]. The organic sulfur will be fully released in combustion – primarily as H₂S and other reduced gaseous species that then oxidize to SO₂. The fate of the sulfur in alkali sulfate is not clear. It may stay connected to the alkali sulfate, but it also may be released due to some decomposition reaction of the alkali sulfate.

In peat and coals part of the sulfur may be present as inorganic minerals. A common example is pyrite (FeS₂). Pyritic sulfur is effectively released in a complex decomposition process and will finally form SO₂:

\[
\text{FeS}_2(s) \rightarrow \text{FeS}(g) \rightarrow \text{Fe}(s) + S(g) \rightarrow \text{FeO}_x(s) + \text{SO}_2(g)
\]

In some waste-derived fuels (sludges) sulfur may be part of the waste processing chemicals such as iron or aluminum sulfates. These also decompose at furnace conditions and release sulfur as SO₃, which further decomposes into SO₂.

![Figure 14.20 Solubility of S in different fuels.](image)
In summary, most of the sulfur in fuels will be released in combustion and finally yield SO$_2$. The only significant exception is calcium sulfate, which may be present in some fuels.

### 14.2.7 Chlorine

Chlorine is present in biomass fuels as chloride salts. These salts may vaporize during combustion as alkali chlorides (KCl$_{(g)}$, NaCl$_{(g)}$) or decompose and release the Cl, which rapidly converts into HCl$_{(g)}$. Most chloride salts in fuels are soluble and show up in the soluble fraction of the leaching test (Figure 14.21).

Some part of Cl may also be present as organic chlorine, such as in waste-derived fuels containing rests of poly(vinyl chloride) (PVC) polymers. The Cl in PVC is insoluble in the leaching test and will stay in the rest fraction.

In most combustion processes all chlorine in fuels is fully released as either chloride vapors (NaCl, KCl, ZnCl$_2$, PbCl$_2$) or gaseous HCl. These primary Cl compounds may undergo several further reactions with other ash-forming matter. The metal chlorides may react with SO$_2$, forming sulfates and releasing HCl. Alkali chloride vapors may also react with quartz particles:

$$2 \text{KCl}(g) + \text{SiO}_2(s) + \text{H}_2\text{O}(g) \rightarrow \text{K}_2\text{SiO}_3(s,l) + 2 \text{HCl}(g)$$

This reaction results in an alkali silicate coating on the bed particle surfaces, and gradually to a risk of bed sintering due to the low first melting point of most alkali
silicates. A similar reaction is possible with other silicates and aluminum silicates. Some of these, for instance kaolin, may be very reactive towards alkali vapors and can be used to purposely absorb alkali chloride vapors from the flue gases.

If alkali chlorides remain in the flue gases without reacting further, they may later, when the flue gas temperature is lower, form particles either by nucleation or by condensing on other colder particles and thus form a part of the fly ash. Fly ashes containing alkali chlorides are known to be much more corrosive than chloride-free fly ashes.

14.2.8 Phosphorus

Phosphorus may be present in biomass fuels as either soluble phosphate salts or in organic molecules containing phosphorus (Figure 14.22). In woody biomass around 3/4 of the phosphorus is inorganic and some 1/4 organic. However, in other biomasses this ratio may be different. In some annual plants the phosphorus content may be very high.

The release and fate of the various phosphorus compounds in combustion furnaces and flue gases is not well studied. However, clearly, both alkali and calcium phosphates may form when fuels containing phosphorus are burned. The former may melt at low temperatures (eutectics) and cause bed sintering or deposit formation. The latter does not appear to cause sintering problems.

Although some studies have been carried out recently, more work is needed to understand the details of phosphorus chemistry in biomass combustion [17–20].

![Figure 14.22 Solubility of P in different fuels.](image)
14.3 Deposit Formation

Deposit formation in a boiler takes usually place either on superheater surfaces or later in the cooler section. Both the ash deposition rate and the properties of the ash deposits are important considering the operation of a combustor. The properties of ash deposits, most important to the successful operation of a boiler, include issues such as the ease of removal from a combustor wall or heat exchanger surface, viscosity, effective thermal conductivity, effective emissivity, deposit strength, elemental composition, morphology, and porosity [21].

The formation of a hard deposit can be described by four most relevant steps:
1) formation of an ash particle,
2) transport of the ash particle or ash-forming compound to a surface,
3) adhesion to the surface,
4) consolidation of the deposit.

After formation of an ash particle as described above the particle is transported to a heat transfer or boiler surface before deposition can take place. Typical transport processes are diffusion, thermophoresis, and inertial impaction. Diffusion and thermophoresis are processes of particle transport in a gas due to local concentration and temperature gradients, respectively. In the case of Fick diffusion, molecules will move to a surface due to a concentration gradient present. Brownian diffusion describes the random movement of small particles. Eddy diffusion describes the diffusion in turbulent systems. In thermophoresis a particle suspended in a fluid with a strong temperature gradient interacts with molecules that have higher average kinetic energies on the side with the hot fluid than on the side with the cold fluid. Diffusion processes are usually important to transport small particles to a surface (<10 µm). The collisions of high energy molecules on the hot side of a particle have more impact than those on the colder side. This gives rise to a net force on the particle. In general, these forces act in the direction opposite to that of the temperature gradient. Inertial impaction is usually the process by which the bulk of the ash deposit is transported to a heat exchanger surface. The rate of inertial impaction depends on target geometry, particle size distribution, and density and gas flow properties. Inertial impaction is important for large particles (10 µm and larger).

After an ash particle hits the surface it may adhere to it. Adhesion can take place by either van der Waals forces or through glueing to the surface. This is possible when a partly molten phase is present that can act as glue between a particle and a surface. When a gaseous ash-forming compound is formed, this could diffuse to the surface and condense directly on the colder surface.

Melting of ash has to be considered far more complex when compared to melting of a single salt. Whereas a single salt may have one melting point, mixtures of ash compounds should be considered as a multicomponent system exhibiting a melting range. This temperature range between the first melting temperature ($T_0$) and the complete melting temperature ($T_{100}$) – also referred to as the liquidus temperature – may be several-100 degrees. The physical state, that is, the share of melt versus solid
material in the particle is dependent on chemistry and elemental composition of the particle and temperature.

To illustrate this, Figures 14.23 and 14.24 show composition diagrams of a two-component salt mixture of typical fly ash components in black liquor combustion,

![Composition Diagram](image)

**Figure 14.23** Composition diagram of a mixture of NaCl with Na₂SO₄.

![Melting Curve](image)

**Figure 14.24** Melting curve for the two-component system 0.8 mol NaCl/0.2 mol Na₂SO₄.
that is, Na₂SO₄ and NaCl. The composition diagram shows that pure NaCl has a melting point of 1073 K while Na₂SO₄ will be molten at 1157 K. Below 900 K both NaCl and Na₂SO₄ will be present as a solid phase. The first melting point may occur at around 900 K \((T_0)\) independent on the salt composition. When raising the temperature even more either a mixture of molten salt with solid NaCl or molten salt with Na₂SO₄ will be formed. The amount of molten phases can be calculated from the lever rule. In the figure an example is indicated for a salt mixture with 80% mol NaCl at ca 1000 K. Here the amount of melt equals:

\[
\frac{(C-B)}{(<C-A)}
\]

The stickiness of ash particles is strongly dependent on temperature and physical state. It has been shown that the presence of a melt in an ash particle acts as a sticking agent for the particle. From an ash stickiness point of view the temperature at which enough melt is present to glue an ash particle to a surface is of major importance. The temperature at which 15% of the condensed phase, that is, the sum of liquid and solid phases, is molten is defined as the critical stickiness temperature in recovery boiler deposits \([22]\). This limit works well for simple ionic salts, but for deposits containing silicon, leading to viscous melts, another criterion is required. Here, the viscosity of a melt could be a criterion for stickiness. If the thickness of the deposit increases the temperature profile within the deposit will change. At a critical thickness the temperature near the flue gas side will have increased so far that the amount of melt in the deposit is such that the deposit starts to flow (slagging) and the deposit will no longer grow in thickness. The amount of melt in a simple salt containing deposit will be some 70% when slagging will occur (Figure 14.25).

There are many approaches to predicting ash deposition. One is the use of indices calculated from the fuel composition. Indices are mainly based on the ash analysis

Figure 14.25 Temperature profiles across a superheater tube wall: (a) clean tube and (b) tube covered with a deposit grown to its steady state thickness.
presented as oxides and were developed to predict deposit formation in coal fired boilers \[23-25\]. An index based on alkaline and alkaline-earth metals has been developed for boilers co-fired by bark, coal, and oil. The portion of sulfate-forming compounds (water-soluble CaO + MgO + Na₂O + K₂O) is expressed as a percentage of the total ash in the fuel fed to the boiler \[26\].

Another method is the determination of the fusibility of ash. With this technique a cone of (laboratory made) ash is heated and the temperature is recorded when the tip of the cone is first deformed (IT); when the cone ash has molten into a spherical lump, with the height is equal to the width (ST); when the height is equal to half the diameter at the base (HT); and when the cone is melted into a layer not more than 1.6 mm high (FT). The method is completely empirical and interpretation of the values obtained is difficult \[27, 28\]. These predictors were the basis for prediction of deposit formation and agglomeration of coal. During the last decade it has become clear that these predictors are poor indicators of ash-related operational problems with biomasses and energy crops \[29-31\].

Ash fusion temperatures as determined from the “whole” fuel ash poorly predict ash deposit behavior when assuming that reactive, mobile ash-forming elements form the initial deposits. Another approach may be purely based on the chemistry and melting behavior of ash-forming compounds. Thermodynamic modeling in combination with chemical fractionation can be used to predict deposit formation of both mono- and co-firing \[32\]. Here the chemical interaction of the volatile ash fractions with the combustion gases can be modeled. By using a smart choice of ash-forming matter data retrieved from standard fuel analyses, chemical fractionation, and information from literature, it is possible to calculate a possible composition of deposits formed during combustion and to predict the melting behavior of this deposit. Based on fuel characterization results ash-forming matter can be divided in either reactive or inert ash-forming matter. Here, for example, silicates are usually considered less reactive whereas soluble alkali, chloride, and sulfur are considered to be reactive and are usually easily volatilized and prone to form volatile species (see above and Figure 14.26).

Figure 14.26 Ash-forming matter in biomass fuels can be divided into reactive and non-reactive parts by laboratory tests. The composition and melting properties of the fly ash formed from the reactive parts of the ash-forming matter can be estimated by multi-component equilibrium calculations \[13\].
At Åbo Akademi University the thermodynamic data used in the calculations are taken from a database, partially developed at the university, for the calculation of reactions related to ash chemistry in combustion and gasification systems. Data from various sources have been combined to give a chemically consistent database for complex phase calculations in systems containing the elements Al, C, Ca, Cl, H, K, Mg, Mn, N, Na, O, P, S, and Si. The database is constituted of 120 gaseous compounds, two liquid solutions, 12 solid solutions and 73 pure condensed phases. In the calculations, carbon, hydrogen, and oxygen are usually taken from the ultimate fuel analysis to make the formation of a realistic gas phase possible. An air factor of 1.2 for the combustion cases and atmospheric pressure is commonly used. The calculations are usually carried out for a temperature range of 500–1200 °C. The ash-forming elements included are supposed to be ideally mixed with the gas phase, allowing formation of carbonates and allowing volatilization of alkali metals. (This can be considered as studying the melting behavior of extremely small particles.)

Figure 14.27 shows an example of results obtained from such calculations. Input data were chosen from the Åbo Akademi fuel database. Figure 14.17a gives the composition of condensed phases, showing the molten phases versus the solid phases. Figure 14.17b gives the amount of molten phase, showing $T_0$, $T_{15}$, and the melting range.

Even deposit formation in co-firing cases can be predicted with thermodynamic calculations by extending the scheme from Figure 14.26 and combining the reactive fractions as determined with the fuel analysis (Figure 14.28). Again, reactive ash-forming matter is used as input in the calculations.

Ash components released from co-fired fuels during combustion may interact with each other and may not behave independently. Either positive or negative effects on deposit formation may be expected in co-firing fuels. In some cases low melting sticky compounds may be formed that make deposit formation worse than expected. In other cases high melting ash may act as a cleaner for heat exchanger surfaces [33–36].

Figure 14.29 shows an example of the interaction of ash-forming matter. Predictions show that a small addition of plywood waste to bark increases the formation of a bothersome fly ash more than expected. A positive effect of co-firing on deposit formation is shown in Figure 14.30. Here the addition of rice husk to bark delayed deposit formation.

Noticeably, thermodynamic calculations assume that the chosen elements/compounds are in equilibrium. This assumption may be true in cases of easily volatile compounds. However, where larger particles, such as Si- and Ca-particles are also present caution is needed when choosing amounts and elements for the calculations and in interpreting the calculation results.

Chemical fractionation alone can also be used to explain the chlorine-content in multi-fuel deposits and the dependencies of different elements and compounds have been shown [37, 38]. It was shown that the Cl-compounds were strongly dependent on the presence of both sulfur and/or Al-silicates (see also reactions in Section 14.5 on corrosion). In these studies no thermodynamic calculations were made, instead
Figure 14.27 Example of thermodynamic calculations for eucalyptus bark: (a) composition of condensed phases, showing molten versus solid phases; (b) amount of molten phase, showing $T_0$, $T_{15}$, and the melting range.
the combination of empirical data from deposit analyses and chemical fractionation together with chemistry was used successfully.

In another laboratory-scale study the release of ash-forming matter from combustion of biomass, such as wood, bark, straw, and waste wood, was investigated.

\[ \text{Figure 14.28} \quad \text{The principle shown in Figure 14.26 can be extended to co-fired fuels; the composition and melting properties of the fly ash formed from the reactive parts of the ash-forming matter from the co-fired fuels can be estimated by multi-component equilibrium calculations [13].} \]

\[ \text{Figure 14.29} \quad \text{Estimation of the percentage of liquid phase as function of temperature for reactive fly ashes produced in co-firing bark with a special type of waste wood in different proportions [13].} \]
Release measurements in a fixed bed and an entrained flow reactor were compared to a combination of chemical fractionation and thermodynamic studies. Laboratory-scale results were even compared to pilot-scale measurements. It was concluded that depending on the interpretation of chemical fractionation release of inorganic matter can or cannot be used for modeling combustion under grate-firing and suspension-firing conditions. Its usability depends on the knowledge available on the combustion processes. [39]. This confirms that, for deposit prediction purposes with thermodynamic calculations, more knowledge about the fuel mixture and its behavior in different conversion processes is needed than only the results from chemical fractionation. However, since the method takes neither physical interactions nor bed reactions of easily volatile elements into account, it can be assumed that the method predicts “the worst case scenario” concerning deposit formation.

14.4 Agglomeration and Sintering in Fluidized Bed Conversion

In the literature terms such as agglomeration, sintering, and de-fluidization are used freely in different ways to describe the unwanted collapse of a fluidized bed.

Here agglomeration is defined as the phenomenon where particles gather into clusters of larger size than the original particles. Sintering is defined as the process in which fine particles become chemically bonded at a temperature that is sufficient for atomic diffusion. Since in fluidized bed conversion bed particles can be held together by a molten phase both the terms agglomeration and sintering can be used to describe the same phenomena. The initial agglomeration temperature is defined as the temperature where the first molten phases appear that are able to “glue” bed particles together into agglomerates. De-fluidization is defined as the total collapse of the fluidized bed resulting in a rapidly decreasing pressure drop or erratic behavior of the
bed, which results in substantial temperature changes. The presence of agglomerates does not, by definition, cause total de-fluidization of the bed. Instead the de-fluidization temperature will still be dependent on boiler-specific conditions as well.

Bed agglomeration is a quite complex phenomenon that can take place in fluidized bed boilers under certain circumstances. Agglomeration cannot only be explained by looking at physical phenomena, such as temperature, particle size distribution, mixing processes with resulting shear stresses between particles, and particle attrition, abrasion, fragmentation and cleavage, but also chemical phenomena will have to be taken into account. An example is the reaction between ash-forming components and bed particles, leading to build-up of a coating and possible agglomeration when molten phases are formed. These molten phases could glue particles together.

In practice both physical and chemical phenomena will work together, leading to bed agglomeration or not.

Bed agglomeration is tightly connected to the release of ash-forming matter (Figure 14.31). It is possible that easily released ash-forming elements would rather condense on bed particle surfaces than form a submicron fume and hence be transported to the flue gas channel. This kind of coating formation has been detected when firing biomass in a quartz bed. It was found that the coating usually does not exceed a thickness of some 10–50 μm for a mean bed particle diameter of 350–500 μm [40]:

1) Ash deposition on bed material is probably dominated by (i) an attachment of small particles to the bed particle surface, (ii) condensation of gaseous alkali species on bed particles, and (iii) chemical reaction of the gaseous alkali on the particle surfaces.

1 Build-up of a potassium rich coating by condensation of gaseous alkali compounds
2 Integration of small fly ash particles such as included minerals and CaSO$_4$ and Ca$_3$(PO$_4$)$_2$
3 Homogenisation and sintering of coating and bed material
4 Alternatively bed material is glued together by molten ash particles

Figure 14.31 Scheme of bed agglomeration, partly adopted from Reference [41].
2) As the continuous deposition on the bed particles proceeds, the inner layer of the coating is homogenized and strengthened via sintering.

3) The melting behavior of the homogeneous silicate layer controls the adhesive forces, which are responsible for the final temperature-controlled agglomeration process [41, 42].

The formation of a coating may initiate:

1) Formation of agglomerates when sticky, that is, partially molten. In this way two different particles can become glued together. The molten phase could be either a viscous glassy silicate melt or a non-viscous melt. The former has been found to be the common reason for bed agglomeration in FBCs using quartz as bed material [30, 43]. A non-viscous melt has been identified occasionally when high sulfur lignites were combusted [44].

2) Chemical reaction sintering the bed particles together forming agglomerates.
This mechanism has been identified in fluidized bed boilers using limestone as bed material. The agglomeration had mainly occurred as a pluggage of the cyclone return leg in a CBC [43].

Neither the chemical interaction between bed material and reactive fine particles nor the less reactive coarse fraction alone can explain the formation of agglomerates. Physical phenomena play a role as well. However, the formation of a coating on bed material is usually a prerequisite for agglomeration and de-fluidization. Analyses carried out by Skrifvars et al. [40] showed which elements are involved, but not where they come from. For a sand bed, silicon found in the coating on the bed particles could originate both from the fuel and the bed particles. Calcium and potassium could originate from the fuels reactive or less-reactive particle fractions. The thickness of the coating formed is a function of chemistry and erosion of the coating due to physical processes.

There are two possible ways to obtain a typical 10 μm thick coating:

1) The coating grows outwards onto the particle, assuming the bed particle act as an inert carrier for the coating material. In this case all elements in the coating come from the fuel and coating formation should occur independently of bed material.

2) The coating grows inwards into the particle. In this case reactive elements could react with the bed particle.

In both cases growth is limited due to either erosion of the coating, diffusion limitation, or both. By comparing the amount of bed material after controlled combustion experiments (i.e., with the amount of bed material before the experiment started and the amount of fuel fed to the combustor) the total weight of coating present can be calculated and distributed over the three main coating-forming elements. After this, the distribution of these elements over the reactive and less-reactive fraction of the ash-forming elements could be combined with the quantity of the elements needed to build up the coating. Up to 60 wt% of the potassium fed to the bed was found in the coatings. This could be introduced by the potassium present in the reactive fraction alone. The rest of the potassium could escape the bed as gaseous...
KCl. Some 8–30 wt% of the calcium present in the fuel ended up in the coatings. This means that up to 92% of the calcium might react to form other components such as CaSO₄. Calcium is divided evenly over the reactive and less-reactive fractions in most biomass fuels. This makes it difficult to determine which fraction is responsible for the calcium found in the coatings. As described above, in wood-derived fuels, calcium is possibly present as included calcite or as oxalate minerals, which are only leached by HCl. Thus, even these calcium minerals are considered reactive when released from the fuel. The calcium leached by water and acetate is supposed to form submicron particles of, for example, CaSO₄ or Ca₃(PO₄)₂. Such components were identified in coatings by SEM/EDX analysis. Even the included “reactive” minerals could be involved in coating formation.

The amount of reactive silicon entering the boiler with the fuel is usually insufficient to form a coating. The less-reactive particle fraction represents in most cases a contamination of sand particles that enter the combustor together with the biomass fuel (or are present in the skeleton of the fuel). Fuel contaminations could act as alternative bed material.

Coating formation could take place by reaction between Si, Ca, and K. In practice components containing these three elements will not coincide. There are two possibilities:

1) Silicon reacts with gaseous potassium to form potassium silicates with a first melting point as low as 750 °C. This could be the first sticky layer formed on bed particles, which catches other small particles released from the fuel such as solid calcium components. After this first capture all components present in the coating could interact, forming a sticky coating and raising the first melting point to some 800 °C.

2) Silicon reacts with calcium first to form calcium silicates with a first melting point of above 1500 °C. This second route is considered unlikely due to the first melting point, making capture of potassium components by glueing impossible at the low temperatures found in FBC. It is found that the first agglomerates occur at some 800 °C [45].

A second way of coating formation on bed material could take place through glueing of bed particles by molten ash available in the bed. When enough molten ash particles are available this could also lead to formation of agglomerates. It may be assumed that in most cases all mechanisms mentioned above will play a role.

Prevention of bed agglomeration has been a major subject of study within fluidized bed combustions. For example, the agglomeration in fluidized beds of, among others, rape and wheat straw, reed canary grass, pine saw dust, pine bark, willow, and Miscanthus has been studied. Al₂O₃ was used as bed material. In addition, laboratory ash was made at different temperatures. The ashes of wheat straw, willow, and Miscanthus prepared at 500 °C showed much higher sintering than when heat treated at 850 °C. In the fluidized bed tests the bed material was not totally agglomerated in any of the cases despite the clear sintering observed in the bed samples [46].
Addition of kaolin produced a shift in agglomeration of bed material to higher temperatures when firing biomass in a laboratory-scale FBC. The results showed that kaolin was transformed into meta-kaolinite particles, which adsorbed potassium species. The increased agglomeration temperature was explained by the decreased fraction of melt in the bed particle coatings [42].

The role of additives such as kaolin and dolomite has also been studied in sintering of straw ash. Again it was found that potassium was captured by kaolin, leading to a higher first melting point. Dolomite added to wheat and barley ash reacted with silica to form calcium and magnesium silicates. No reactions between potassium and dolomite could be detected [47].

In predicting bed agglomeration the behavior of the fuels and their interaction with bed material are of major importance. When considering bed agglomeration all ash-forming elements present in the fuel should be taken into account. The reactive elements could play a role in the formation of a coating on the bed material, whereas less-reactive material could become trapped in a sticky coating. Thus, when modeling bed agglomeration the entire fuel should be taken into account and not only a reactive or less reactive fraction as used for predicting deposit formation. In this way the thermodynamic calculations could simulate the interaction of all ash-forming elements with the bed material [48].

Modeling of the agglomeration tendency of biomass fuels under reducing conditions and oxidizing conditions revealed no large differences between combustion and gasification cases. With gasification, reduced species are formed that could have a higher volatility and lower first melting point than those formed by combustion [49, 50].

14.5 Corrosion

Corrosion of heat exchanger surfaces is one of the most unwanted and costly phenomena that can occur in a boiler. With the desire to reach higher steam temperatures in an attempt to raise energy efficiency and the current trend of changing to alternative fuels often containing alkali metals and chlorine, high-temperature corrosion may be a real challenge.

Corrosion in biofuel and waste fired boilers is usually caused by high temperatures in combination with solid deposits containing chlorine and sulfur in different forms (Na, K, Zn, Pb, etc.). These compounds cause degradation of the superheater materials mainly due to metal oxidation. Accordingly, corrosion as described here may be defined as unwanted oxidation of heat exchanger surfaces by interaction with chlorine-containing fly ash and/or gaseous compounds.

The degree of corrosion depends on the superheater material, steam temperature, deposit composition, and flue gas composition. Several types of steels are used; mostly they are based on iron, chromium, and nickel in different amounts, with smaller shares of molybdenum and some other elements. All metals have a protective oxide layer on the metal surface. This oxide layer is usually very thin (5–10 nm) and dense
and prevents any further oxidation of the metal. However, at higher temperatures this oxide layer behaves differently in different alloys and some may lose their protectiveness as a result of these conditions (deposit and gaseous compositions). Generally, the corrosion resistance of a material can be ranked according to its amount of Cr and Ni. The higher the content of Cr and Ni the better the corrosion resistance usually is. There are exceptions, which are dependent on the prevailing conditions.

Chlorine induced corrosion is usually related to either formation of gaseous hydrochloric acid, gaseous chlorine, gaseous alkali chlorides, or deposition of alkali chlorides on tube surfaces. Alkali chlorides present in a deposit lower the melting temperature range and hence worsen corrosion. If the fuel also contains sulfur, the residence time is long enough, and the temperature in the combustion zone is high, gaseous alkali chlorides are converted into sulfates before being deposited on the tubes. In this case corrosion is limited because the formation of a melt is small at typical tube metal temperatures due to the higher melting temperature of the alkali sulfates [51].

The situation would become more complicated when the alkali chlorides do not become sulfated completely before reaching the tubes. In this case chlorine induced corrosion may take place.

Although, there are several theories on the mechanisms of corrosion reactions taking place at a heat exchanger surface, the outcome is still debatable. Several theories involve alkali metals and chlorine. Mechanisms have been described in several different studies (e.g., References [51–53]) and it is commonly agreed that chlorine either in gaseous form or in ionic form penetrates the protective metal oxide layer, where it reacts with metallic iron to produce iron chloride (FeCl₂) that can be formed under the reducing conditions under the oxide scale. Iron chloride has a relative high vapor pressure and may evaporate continuously from the metal–scale interface and diffuse outwards through the scale. At the same time the oxygen partial pressure increases, which enables the iron chloride to oxidize to iron oxide (Fe₂O₃ or Fe₃O₄) simultaneously releasing chlorine that either follows the flue gas flow or diffuses back through the material and may continue the degradation reaction of the material.

Whereas NaCl is a cause for corrosion in coal fired boilers, KCl is more relevant for biomass fired boilers. During combustion gaseous alkali chlorides may be produced that form a deposit of fine condensed fly ash situated close to the superheater surface. It was shown above that a molten fly ash may form deposits. Obviously, a molten (even partially molten) phase enhances contact between the deposit and a metal surface, facilitating interaction of ash compounds with the metal surface and may thus enhance corrosion reactions.

Corrosion occurring above T₀ is called super T₀-corrosion, that is, corrosion that occurs at temperatures above the first melting temperature of the fly ash deposited [53].

Deposits containing alkali and chloride often show a low first melting temperature. Compared to alkali sulfates, addition of small amounts of chloride may lower the first melting temperature to 628°C. A further addition of chloride will
then increase the amount of melt, but will not lower the first melting temperature any further. The first melting point may be lowered even more when more potassium would be present in the deposit. A $T_0$ as low as 522°C may be encountered, making such a deposit sticky at low temperatures. This dramatic decrease in first melting temperatures is not encountered in chlorine-free deposits [53].

Figures 14.32 and 14.33 show examples of laboratory-scale studies [53]. In these studies metal alloys were covered with synthetic fly ash of known composition and melting behavior, after which the plates were exposed to a gaseous atmosphere at elevated temperatures. SEM/EDX analysis of the metal surface and the “fly ash” salt layer make a statistical analysis of corrosion possible. The figures show the impact

![Figure 14.32](image)

**Figure 14.32** SEM/EDX analyses of laboratory-scale corrosion tests [53].

![Figure 14.33](image)

**Figure 14.33** Corrosion after exposure to alkali salts at various temperatures. Exposure time: one week. (a) 90/10 mixture of sodium and potassium sulfate with no chloride. (b) 90/10 mixture of sodium and potassium sulfate with 1.3% chloride [53].
of a decrease in first melting point by addition of potassium and chlorine to the synthetic ash mixture. The corrosion even started at lower temperatures than the $T_0$, clearly showing that corrosion is not only limited to systems with molten deposits. Presence of small amounts of sodium and potassium chlorides may initiate corrosion.

The presence of zinc chlorides as formed during combustion of waste-derived fuels has been shown to enhance corrosion reactions as well. ZnCl$_2$ decreases the first melting point compared to pure alkali sulfates. Deposits containing these compounds may thus be molten at low temperatures, and show heavy corrosion in laboratory-scale tests [54]. Thermodynamic calculations have shown that ZnO is stable phases expected to be formed at high temperatures, even when chlorine would be present. This indicates that ZnCl$_2$ may become oxidized, thereby freeing chlorine. Depending on the amount of SO$_2$ present, alkali chlorides or HCl may be formed [55].

Although bothersome, corrosion can sometimes be prevented. If the conditions (deposit and/or flue gas compositions) are very difficult the only way to prevent corrosion is by keeping steam temperatures low, sometimes as low as some 480°C, as in recovery boilers. However, it has been shown that when formation of alkaline chlorides can be reduced high-temperature corrosion can be minimized. In some cases the ash chemistry can be influenced by use of additives. Such additives can be elemental sulfur, “chlorout,” that is, (NH$_4$)$_2$SO$_4$ [56], Al$_2$(SO$_4$)$_3$ or Fe$_2$(SO$_4$)$_3$ [57], and kaolin added to bed material in fluidized bed combustion [58]. The sulfur additives, when injected will decompose when heated and the sulfur reacts with alkali chlorides to produce solid alkali sulfate and gaseous HCl, which follows the flue gases out from the boiler, while the kaolin reacts with the alkalis to produce alkali-aluminosilicates and HCl:

$$\text{(NH}_4\text{)}_2\text{SO}_4(\text{aq}) \rightarrow \text{SO}_3(g) + 2\text{NH}_3(g) + \text{H}_2\text{O}(g)$$

$$2 \text{KCl}(g) + \text{SO}_3(g) + \text{H}_2\text{O}(g) \rightarrow \text{K}_2\text{SO}_4(s) + 2\text{HCl}(g)$$

$$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2(s) + 2\text{NaCl}/\text{KCl}(g) + \text{H}_2\text{O}(g) \rightarrow \text{Na}_2/\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(s) + 2\text{HCl}(g)$$

In some cases these effects can also be achieved by co-firing different fuels in the right shares; for example, biomass and peat [38], where the sulfur in the peat can prevent the formation of chlorine-containing deposits, or bark and sewage sludge, where both the sulfur and aluminosilicates in the sludge hinder the formation of alkali chlorides [37, 59].

14.6 Final Remarks

This chapter has been dedicated to more challenging fuels like biomass derived fuels that nowadays are used as a replacement for coal. Examples were taken from 92 fuels
extracted from the Abo Akademi fuel database, a collection of advanced fuel analyses carried out at Abo Akademi University during the last decade.

Deposit formation, that is, fouling and slagging, corrosion, and sintering, are often cause for unwanted shut downs of boilers. These problems are ash related. Besides physics, chemistry plays an important role in explaining and predicting the above-mentioned phenomena. During the last few decades it has become clear that ash properties are heavily dependent on the way ash-forming matter is present in a fuel and process conditions. It was shown that different analytical methods, for example, chemical fractionation and SEM/EDX of fuels, can give valuable information.

When considering the chemistry behind deposit formation, deposit formation may be predicted by predicting the melting behavior of ash. This chapter has introduced the concept of stickiness ($T_{15}$) and melting range. Extensive fuel characterization in combination with thermodynamic equilibrium calculations can be used to find the possible melting range of the ash. This concept may also be used when co-firing fuels. However, all the interacting effects of different fuels cannot be explained and more research is needed to explain both positive and negative interactions of ash mixtures.

In addition, in agglomeration the stickiness of ashes plays an important role. Interactions with bed material may lead to formation of low melting silicates causing agglomeration. Depending on other process parameters this may lead to complete shut-down of a fluidized bed boiler. In recent years, the mechanism behind alkali induced agglomeration has been solved. However, it was shown that phosphorus may also be involved in agglomeration. More studies are needed before the mechanism of phosphorus-involved agglomeration is solved.

High-temperature corrosion mechanisms are still under debate. In almost all corrosion cases the presence of chlorine has been the cause of corrosion. In most cases the first melting point ($T_0$) is decisive in determining whether corrosion will occur. In some cases, though, even sub-$T_0$ corrosion has been found.

Combustion of biomass, especially wood-derived fuels, may lead to exhaustion of forest soils and subsequent lower productivity. This will be a challenge for the future to retain forest fertility by either reusing ash from wood-derived fuels or introducing ash reuse of other fuels burned. In the future more studies will be carried out on the re-usability of these alternative ashes and ashes originating from co-firing.

References


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