



FOULING & CORROSION OF COAL-FIRED BOILER

Coal contains various impurities, called ash components, the characteristics and amounts of which are dependent on the location of the coalmine. The main chemical elements are as follows:

Sulfur (S):

Sulfur is contained mainly in the form of iron sulfides, chiefly FeS_2 , organic compounds combined with the original coal substances, and sulfates such as CaSO_4 and FeSO_4 . FeS_2 is usually decomposed in to iron oxides and sulfur oxide in the combustion process. When it is burned in a reducing atmosphere due to a deficient air supply, however, the decomposition does not proceed completely and FeS is produced. Fe-S and iron interact and form a eutectic mixture having a low melting point, so that slagging often occurs and causes problems in the fire bed in the case of stoker firing. In general, though, the sulfur component of Fe-S is released completely and reacts to form SO_2 , which is further oxidized in part to SO_3 and induces low temperature fouling and corrosion.

Alkali Metal Elements (Na, K):

These are the most important impurities with regards to fouling. They react with SO_3 , and produce sulfate compounds. In the case of coal containing very little sulfur, they form carbonate compounds, which also deposits directly on to HTS when the SO_3 content is too low to change all of the NaCl to sodium sulfate.

Phosphorus (P):

Most of the phosphorus contained in coal is believed to exist as the fluoride of calcium phosphate, $\text{Ca}_5\text{F}(\text{PO}_4)_3$. This changes to the stable calcium phosphate in an oxidizing atmosphere. But in a reducing atmosphere such as in stoker firing, it changes to a phosphorus oxide having a low melting point, which induces slagging troubles in some cases. Phosphorus would contribute, therefore, very little to fouling in the case of pulverized coal firing.



Other Elements (Si, Al, Ti, Fe, Ca, Mg, etc.):

Most of the impurities in coal, that is, the ash component, consist of the elements silicon, aluminum, titanium, iron, calcium, magnesium, and so on, and therefore fly ash and slag, which are main ingredients of combustion products, are also composed of them. Characteristics such as melting point and viscosity of slag and ash are dependent on the composition of these elements.

Fly-ash particles collide with HTSs by their inertial force, these colliding fly-ash particles can adhere and deposit on HTS when one or more of the following conditions are satisfied, that is:

- The ash particle is in a molten state;
- The deposition surface of HTS, is covered by some molten salt;
- The deposition surface is covered with some substance that becomes molten the instant an ash particle collides with surface.

Judging from these conditions, layers formed by deposition of Na_2SO_4 and /or K_2SO_4 in the molten or nearly molten state would contribute to catching colliding particles. Similarly, sulfates of sodium and potassium and fly ash deposit on to the HTS and develop the second layer further. As the second layer increases in thickness and its surface temperature rises beyond the saturation temperature of Na_2SO_4 and K_2SO_4 , these sulfates would stop condensing on to the HTS. After that, only fly ash would be deposited and would grow a layer.

Serious fouling will be developed if the fly ash carried by the gas is in a molten state. The combustion gas temperature at the inlet of the SH and / or RH section should therefore be designed with careful attention to the melting characteristics of fly ash.

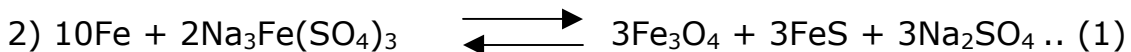
Low-temperature corrosion is mainly caused by sulfuric acid under the same mechanism as in oil-fired boilers. There are two main mechanisms; sulfidation attack due to alkali sulfates of sodium and potassium, and corrosion caused by complex compounds of the sulfates $\text{Na}_3\text{Fe}(\text{SO}_4)_3$, and $\text{K}_3\text{Fe}(\text{SO}_4)_3$, which are formed by alkali sulfates and Fe_2O_3 contained in fly ash. For coal-fired boilers, the latter mechanism is more important than the former.



Na₂SO₄ and / or K₂SO₄ and Fe₂O₃ deposited on to HTSSs react with SO₃ contained in combustion gas and form complex compounds, as described by the following equation:



These complex compounds are apt to become molten due to their low melting points and attack the iron material of HTSSs, that is,



Fe-S in the right-hand side of the above equation is reduced to Fe₃O₄ and SO₃ by further reactions, and Na₂SO₄ repeats the reaction process of equation 1 above. Thus complex compounds of Na₃Fe(SO₄)₃, K₃Fe(SO₄)₃, and Fe-S advance the above corrosion process cyclically. The complex compounds are not formed in the high-temperature region beyond 1300°F (704°C). That is why the corrosion rate decreases abruptly when the temperature reaches this level.

Corrosion due to fly ash is one of the gas-side problems troubling coal-fired boilers. Solid or liquid particles in the gas flow collide with the HTS and / or structural members and erode or injure those surfaces mechanically. Quantitative estimation of erosion is not easy since it is difficult to clarify the mechanism of erosion. A general relation has been derived empirically as follows:

$$E = k \cdot V^n \cdot f(\theta)$$

Where E is the mass ratio of eroded material to the total mass of colliding particles and V is the velocity of a colliding particle. The constant K, which is almost independent of material properties, takes a value ranging from 1 to 10, and the exponent n takes a value ranging from 1 to 2 when V is measured in m/s. f(θ) is a non-dimensional factor expressing the effect of the collision angle θ, with a maximum value of 1. f(θ) becomes maximum at about θ = 20° for ductile materials and 90° for brittle materials.

There is a possibility that a soot blower induces erosion troubles in coal-fired boilers since its strong jet entrains and accelerates the surrounding gas containing fly ash.



Countermeasures Against Gas-side Fouling & Corrosion

Low-temperature fouling and corrosion, and also Na_2SO_4 production, are mainly dependent on the content of SO_3 that is produced in the combustion area. To inhibit SO_3 production by low excess air combustion, therefore would be an effective means of preventing gas-side fouling and corrosion. Low excess air combustion is also effective against V_2O_5 production.

Additives

Various additives have been tried and/or used practically for many years and to change harmful combustion products to other, chemically harmless compounds, and to prevent fouling and corrosion. Among them, magnesium chemicals such as MgO and $\text{Mg}(\text{OH})_2$ have been recognized both practically and theoretically as being the most effective, especially for high-temperature fouling and corrosion. When magnesium chemicals are added to the combustion zone of the furnace, they react with vanadium oxides and form magnesium vanadates such as $3\text{MgO} \cdot \text{V}_2\text{O}_5$, which has a very high melting point of 1191°C . Magnesium chemicals also react with SO_3 and convert it to harmless magnesium sulfate, MgSO_4 .

To attain the desired effects of magnesium additives, however, careful attention should be paid to the selection of an appropriate method of injection into the combustion zone. It is recommended to spray magnesium additives into the combustion zone in the form of fine particles. The amount required is about three times the molar ratio of magnesium to vanadium. It should be noted, however, that magnesium additives are effective mainly for oil-fired boilers but not as effective for coal-fired boilers, especially in the temperature range beyond 700°C where the corrosion caused by alkali sulfate becomes dominant. **No effective additive has yet been developed for coal-fired boilers.**



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