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Effect of chemical additives on hard deposit formation and ash composition in a commercial circulating fluidized bed boiler firing Korean solid recycled fuel

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ABSTRACT

Combustion of SRF (solid recycled fuel) and biomass with potassium (K), sodium (Na), and chlorine (Cl) contents can result in operational problems such as hard deposit formation and convection pass tube corrosion. Two types of commercially available chemical additives, ammonium sulfate [$(NH_4)_2SO_4$] and borax solution, were examined to elucidate their effect on hard deposit formation and the particle composition of fly ash on the convection pass of a commercial CFBC (circulating fluidized bed combustion) boiler. The addition of ammonium sulfate/borax solution hindered metal chloride formation and reduced the amount of hard deposit formation on the convection pass tubes. Both the alkali and potassium chloride content and the point load hardness of the hard deposit were reduced, while the melting temperature increased according to the borax solution use. When chemical additives were employed, the particle size distribution of the fly ash shifted to coarse particles. In particular, SEM (scanning electron microscopy) images of the fly ash particles revealed the attachments of fine particles to the ash particles. These were assumed to be mineral salts attached to the coarse particles, which increased the overall particle size distribution.

1. Introduction

Thermal energy utilization, i.e., the combustion of biomass and SRF (solid recycled fuel) is an important measure to comply with climate control and CO_2 reduction. Many new boilers are built to use solid fuel made of biomass and SRF. Particularly, the energy conversion of biomass is an effective solution for the carbon reduction market (e.g., Certified Emission Reduction). The operation and production costs of waste-to-energy conversion are relatively cheaper than those of other renewable energy technologies. This effect is direct and substantial. Thus, the market can adapt to the technology in a relatively short period when conventional energy facilities utilize SRF mixing with existing fuels.

However, SRF contains high concentrations of harmful minerals that can affect both the facilities and environment. Notably, chemicals comprising alkali (Na, K) and alkaline earth (Mg, Ca) metals, sulfur (S), and halogens (Cl) are known to be significantly harmful [1,2]. At flue gas temperatures < 500 °C, Zn and Pb combine with chlorides to form mineral chlorides, while sodium and potassium chloride (NaCl and KCl) and sulfate (Na_2SO_4 and K_2SO_4) are formed at temperatures > 650 °C. These compounds combine with fly ash to form hard deposits on the superheater tubes of the boiler [3]. Most hard deposits form at the high temperature zone on the upper part of the convection pass of the boiler. Hard deposits formed by mineral chloride bonding are hard and non-porous [4]. These hard deposits block heat transfer from the hot gas to the steam tube by reducing heat transfer, thereby lowering the efficiency of the boiler. Moreover, hard deposits are a major concern in tube corrosion since chlorides tend to migrate from the hard deposit to the bare metal and become attached to the steam tubes [5,6]. When the deposit continues to grow on the tube surface, it eventually blocks the passage of the flue gas and increases the system draft pressure, one of the major reasons for irregular plant shut down and premature maintenance.

Previous studies have reported on the effect of NaCl and KCl on superheaters comprising metals from different classes [7–9]. NaCl and KCl displayed equivalent corrosiveness on the surfaces of all the test

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metal specimens. Many studies on the ash fusion temperature and ash formation mechanism have been reported in the literature [10–12]. However, studies on the characteristics of hard deposit formation at different locations of a convection pass are rare, particularly those on the control effect in commercial-scale SRF-burning boilers. To date, few chemical additives that can suppress steam tube corrosion in boilers by controlling hard deposit formation have been reported [15]. Studies on the effect of ammonium sulfate on a large-scale biomass-burning CFBC boiler have revealed that the overall performance was improved when ammonium sulfate was employed. This significantly lowered both the amount of KCl in the flue gas and that of fine particles. They also reported that the Cl, K, and Na contents were higher as the particle size became finer and thus, the fine particles consisted mainly of Cl and K [13–15]. Overall, the effect of the chemical agent has been explained in the literature; however, the effect of a chemical agent on a local position is yet to be established.

This study focused on the physical property changes caused by chemical additives employed to reduce hard deposits. The two chemicals that are currently employed in commercial SRF-burning boilers, namely ammonium sulfate and borax solution, were tested on a 10-MWe-scale commercial SRF-burning CFBC boiler. The aim of this study is to qualify the effect of chemical additives on the formation and property changes of hard deposits. The hard deposit samples were classified according to their location in a convection pass with varying flue gas and steam temperatures.

2. Material and methods

2.1. Fuel

Table 1 presents the analysis of fuel samples used for the 10-MWe SRF-burning CFBC boiler. Two types of fuels were employed: RDF (refuse-derived fuel) made from municipal solid waste and RPF (refuse plastic fuel) made from waste plastics. Proximate analysis revealed that RDF comprised a moisture content of 10.7%, a combustibles content of 75.2%, and an ash content of 14.1%, while RPF contained a moisture content of 7.4%, a combustibles content of 80.4%, and an ash content of 12.2%. The higher heating values of RDF and RPF were 5180 kcal/kg and 7560 kcal/kg, respectively, based on the as-received samples. Ultimate analysis indicated respective carbon, hydrogen, nitrogen, oxygen, and sulfur contents of 49.91, 7.01, 1.21, 33.22, and 0.36% for RDF and 56.28, 7.81, 0.52, 8.28, and 0.16% for RPF, based on the dry and ash-free state. The RDF and RPF ash comprised 3.9 and 9.7% Cl contents, respectively, and 1–3 wt% Na and K. The RDF/RPF mix ratio was 50:50 during combustion.

Table 1
Fuel properties: proximate analysis, ultimate analysis, and ash compositions of fuels burned in the CFBC (circulating fluidized bed combustion) boiler.

Parameter	RDF	RPF
Proximate analysis (wt%, as-received)		
Combustibles	75.2	80.4
Moisture	10.7	7.4
Ash	14.1	12.2
Ultimate analysis (wt%, daf)*		
C	49.9	56.3
H	7.0	7.8
N	1.2	0.5
O	33.2	8.3
S	0.4	0.2
Heating value (kcal/kg)		
Lower heating value	4,220	6,570
Higher heating value	5,180	7,560
Ash compositions of fuels (wt%)		
Na	2.0	2.8
Mg	1.1	1.8
Al	5.8	9.8
Si	8.9	15.7
P	0.4	0.7
S	0.6	0.7
Cl	3.9	9.7
K	1.0	2.8
Ca	8.9	27.6
Ti	4.6	18.2
Cr	14.1	0.2
Mn	1.5	0.4
Fe	41.7	7.8
Co	0.2	0.1
Ni	3.5	0.1
Others	1.2	0.7

* daf: dry-ash free.

2.2. Additives

Two types of well-known commercial additives were tested on the commercial CFBC boiler, namely, ammonium sulfate and borax solution. Borax solution has been acknowledged to soften hard deposits and block chloride deposits on the bare tube surface [17]. The Na/K salt forms during combustion when a fuel with high Na and K contents is used in the boiler. This salt is in vapor form at the high temperatures of the convection pass inlet. Subsequently, the molten salt combines with fly ash and sticks to the superheater tubes forming hard deposits. Even worse, the chloride in the hard deposit migrates into the bare tube metal and corrodes the metal. A 37% solution of ammonium sulfate was injected in the duct between the cyclone and convection pass to test the sulfide substitution effect on the metal chloride [13]. One advantage of ammonium sulfate is that it can simultaneously reduce KCl and NOx emissions. Thus, ammonium sulfate can replace the conventional additives, ammonia (NH_3) and urea, to produce the selective non-catalytic reduction (SNCR) of NOx [15]. The known mechanism of ammonium sulfate is the reaction with sodium and potassium chloride and the switching of the chloride to the sulfate Eqs. (1) and (2) [14,15]. The latter compound has a higher melting temperature and exists as a solid in the convection pass inlet. This reduces hard deposit formation in the superheater tubes.

$$(NH_4)_2SO_4(aq) \rightarrow 2NH_3(g) + SO_3(g) + H_2O(g) \quad (1)$$

$$SO_3(g) + 2(K/Na)Cl(g) + H_2O(g) \rightarrow (K/Na)_2SO_4(s) + 2HCl(g) \quad (2)$$

On the other hand, the borax solution comprised 10 wt% $Na_2B_4O_7{\cdot}10H_2O$ (borax), an oxygen supply agent, and a solvent (hydrogen peroxide, sodium hydroxide, or water) [16]. Borax is widely employed as an inhibitor of cement agglomeration and as flux in metallurgy [17]. It attaches to the metal surface and blocks any contact between the metal and oxygen atoms. The mechanism is not clearly known; however, in this study, when the borax solution was injected with the fuel into the system, it reacted with the salt vapor and solidified it at the convection pass temperature. This reaction also reduced hard deposit formation and softened the hard deposit. The compositions of ammonium sulfate and the borax solution are presented in Table 2.

Table 2
Additive compositions.

Ingredients, Conc. %	Ammonium sulfate solution	Borax solution
Water	73	73.5
Ammonium sulfate/Borax	37/0	0/10
Polyol	–	13
Sodium hydroxide	–	3.5
Potassium hydroxide	–	1–2
Hydrogen peroxide	–	5–7