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Published in:
Impacts of Fuel Quality on Power Production

Publication date:
2016

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Laxminarayan, Y., Jensen, P. A., Wu, H., Bøjer, M., Jappe Frandsen, F., & Glarborg, P. (2016). Deposit Shedding in Biomass-fired Boilers: Shear Adhesion Strength Measurements. In Impacts of Fuel Quality on Power Production

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Deposit Shedding in Biomass-fired Boilers: Shear Adhesion Strength Measurements

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ABSTRACT: Ash deposition on boiler surfaces is a major problem encountered during biomass combustion. Ash deposition adversely influences the boiler efficiency, may corrode heat transfer surfaces, and may even completely block flue gas channels in severe cases, causing expensive unscheduled boiler shutdowns. Therefore, timely removal of ash deposits is essential for optimal boiler operation. In order to improve the understanding of deposit shedding in boilers, this study investigates the shear adhesion strength of biomass ash deposits on superheater tubes. Artificial biomass ash deposits were prepared on superheater tubes and sintered in an oven at temperatures up to 1000 °C. Subsequently, the deposits were sheared off by an electrically controlled arm, and the corresponding adhesion strength was measured. The results reveal the effect of temperature, deposit composition, sintering duration, and steel type on the adhesion strength.

Keywords: biomass, ash, soot-blowing, corrosion, boiler, adhesion

1. Introduction

One of the major operational problems encountered in biomass-fired boilers is the formation of ash deposits on boiler surfaces, thereby hindering efficient heat transfer to the steam cycle [1]. Ash deposition may completely block flue gas channels in severe cases, causing expensive unscheduled boiler shutdowns. Furthermore, ash deposits may cause severe corrosion of boiler surfaces [2]. Therefore, timely removal of ash deposits is essential for optimal boiler operation.

Natural as well as artificially induced shedding of ash deposits may be caused by several mechanisms including erosion, debonding, molten slag flow, and thermal and mechanical stresses in the deposits [3]. Debonding is the dominant mechanism for shedding of dense and hard deposits in biomass boilers, occurring when the generated stress (e.g. by soot-blowing or due to the inherent weight of the deposit) exceeds the adhesion strength at the tube-deposit interface [1]. Hence, quantification of the adhesion strength of ash deposits is crucial for understanding deposit shedding and for optimizing artificial removal of deposits (e.g., by soot-blowing).

The objective of the present work is to quantify the shear adhesion strength of biomass ash deposits on superheater tubes under different deposit properties and boiler conditions to determine the effect of gas and steel surface temperature, deposit composition, sintering duration, steel type and thermal shocks.

Apart from providing a better fundamental understanding of deposit shedding, the outcome of this study will facilitate boiler operation by recommending boiler conditions for minimizing the formation of strong deposits. Furthermore, the data obtained from this study may be used to optimize soot-blowing in boilers.

2. Experimental work

Replication of biomass-fired boiler deposits has been attempted in this study, by preparing artificial deposits using fly ash particles obtained from biomass-fired boilers as well as model fly ash compounds, sintered on superheater tubes. The deposits are allowed to heat up and sinter inside an oven at a specified temperature, under air flow. Higher sintering temperatures are used to simulate the deposit formation process, since the fly ash is at a higher temperature before condensing on the tubes. In order to obtain tightly packed and adherent deposits, the ash particles were mixed with a 50% isopropanol solution to prepare a thick slurry, and moulded into a cubical shaped deposit on the surface of the tube, using a Teflon mould.

Experimental analysis was carried out using pure KCl (Sigma Aldrich), as well as fly ash obtained from a straw-fired grate boiler, a wood-fired suspension boiler, and a straw+wood co-fired suspension boiler. The properties of the fly ashes are provided in Table 1. Additionally, model fly ash deposits (average particle size- 61 μ m) were prepared using KCl, K₂SO₄, K₂CO₃, CaO and SiO₂ to understand the effect of different components constituting typical fly ashes. TP347HFG steel tubes (Salzgitter Mannesmann) were used for the experiments. The tubes were pre-oxidized for 24 hours at 600°C in order to better replicate operational boiler tubes.

The artificial deposits were allowed to sinter inside the oven for a fixed duration, followed by shear strength measurements at a specified temperature, where an electrically controlled arm was used to de-bond the artificial deposit from the superheater tube, as shown in Fig. 1. The arm was controlled using a linear actuator, and the corresponding force applied on the ash deposit was measured using a load cell. In order to account for the scatter observed while measuring adhesion strength, measurements were conducted on at least 4 deposit samples for each instance of experimental conditions.

Tab. 1: Composition particle size and melting point analysis of the investigated fly ashes

Elemental composition (wt. %, dry basis)	Straw fly ash, grate fired	Straw+wood co-fired fly ash, suspension fired	Wood fly ash, suspension fired
Al	--	2	2.13
Ca	1.3	20	20.8
Cl	19	1.3	0.2
Fe	0.044	1.4	1.73
K	43	9.1	6.26
Mg	0.12	3.3	3.22
Na	0.9	0.9	0.43
P	--	1.4	1.09
S	7.9	1.5	1.08
Si	1.1	12	17.7
Ti	--	0.14	--
Mn	0.059	--	--
Softening temperature (°C)	640	1240	1220
Hemispherical temperature (°C)	640	1250	1230
Fluid temperature (°C)	760	1260	1240
Median particle size (μ m)	51.7	44.5	34.7

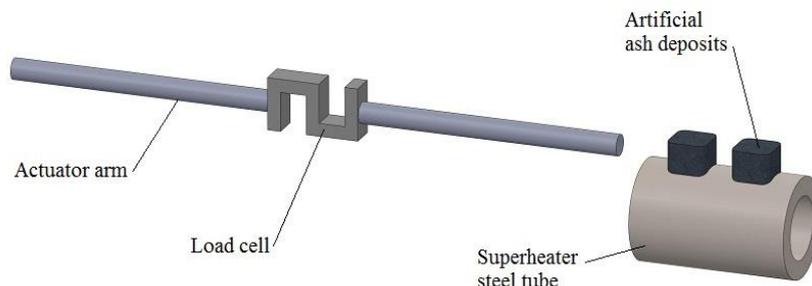


Fig. 1: Experimental setup for adhesion strength measurements. The superheater steel tube is placed inside the oven while the load cell is outside the oven. The actuator arm shears off the artificial ash deposit and the load cell measures the corresponding adhesion strength.

3. Results

3.1. Effect of deposit type and sintering temperature

Fig. 2 shows the effect of sintering temperature on adhesion strength. Experiments were performed with pure KCl, as well as the 3 different boiler fly ashes (see Table 1). It can be observed that adhesion strength increases with increasing temperature, with a sharp increase near the melting point/ ash softening temperature [4], i.e., 640 °C for straw fly ash and 770 °C for KCl. This is due to the formation of a dense, partially molten layer at the interface, as seen in Fig. 3. As the temperature increases, corrosion starts to occur at the interface. As a result, corrosion products, such as Fe/Cr chlorides, oxides, chromates, etc. are formed [2, 5, 6, 7, 8, 9]. Most of the corrosion products form a complex eutectic mixture with the components present in the deposit [10]. This leads to a lower eutectic temperature at the interface, compared to the outer layers of the deposit. The partially molten layer causes increased surface wetting and adsorption [11], leading to high surface adhesion.

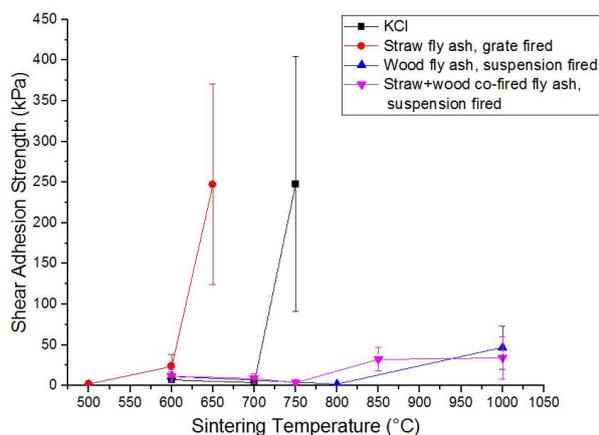


Fig. 2: Effect of sintering temperature on shear adhesion strength for KCl and different fly ashes. Shear adhesion strength increases sharply near the melting point/ash softening temperature. Deposits sintered for 4 hours, measured at 600 °C, steels pre-oxidized for 24 hours, average of 4 data points

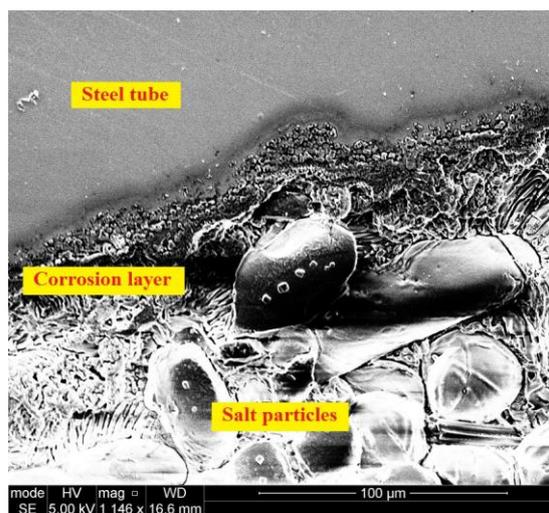


Fig. 3: SEM image of deposit-tube interface. KCl-K₂SO₄ (50 wt%) deposit, sintered at 650 °C for 4 hours, steel pre-oxidized for 24 h.

A sharp increase in adhesion strengths for wood fly ash and the straw+wood co-fired fly ash has not been observed in this study, due to their high ash softening temperatures, 1220 °C and 1240 °C respectively (see Fig. 2).

In order to better understand the relationship between the partially molten layer at the interface and adhesion strength, experiments were performed with model fly ash compounds containing KCl and K₂SO₄. The amount of K₂SO₄ in KCl was varied, and the corresponding results are shown in Fig. 4, along with the KCl-K₂SO₄ phase diagram.

The results indicate that while pure substances do not have much adhesion strength at 650 °C, mixing the components causes a large increase in the adhesion strength. Since KCl and K₂SO₄ form a eutectic mixture, mixing the components causes an increase in the melt fraction of the deposit at temperatures above the melting point. As mentioned previously, the eutectic temperature of the deposit at the interface is lowered due to the formation of corrosion products.

Therefore, it can be inferred that higher melt fraction at the deposit-tube interface leads to higher adhesion strengths, as suggested by Fig. 4.

3.2. Effect of sintering time

Sintering time seems to have a negligible effect on adhesion strength up to 24 hours at the conditions investigated, as seen in Fig. 5. It should be noted that the experiment corresponding to 0 hours of sintering time involves 30 min of heating time and 5 minutes for strength measurement at 600 °C.

The results suggest that the initial, partially molten corrosion layer is formed rather quickly, and significant changes in adhesion strength do not occur after the formation of the initial corrosion layer at the interface within 24 hours. Several corrosion studies in literature indicate that the rate of corrosion decreases considerably over time [2, 5, 12]. The change in melt fraction brought about by increasing corrosion is probably not significant enough to observe reliable changes in adhesion strength. However, further investigation is required prior to arriving at conclusions.

Nevertheless, an increase in the adhesion strength may be observed in boilers due to sintering caused by other reactions occurring in the deposit, e.g., sulphation [13], which have not been investigated in this study. Sulphation does not occur in the experimental setup, due to the absence of SO₂ in the gas stream.

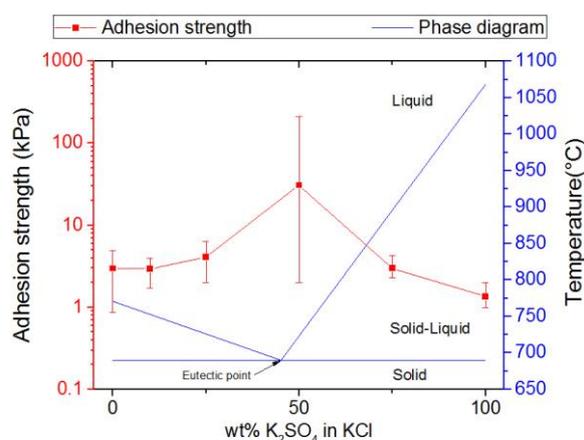


Fig. 4: Effect of varying concentrations of K₂SO₄ in KCl on adhesion strength. Deposits sintered at 650 °C for 4 hours, measured at 600 °C, steels pre-oxidized for 24 hours, average of 4 data points (24 for 50%)

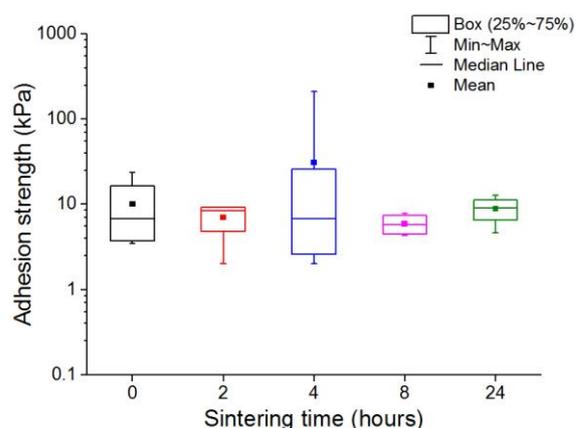


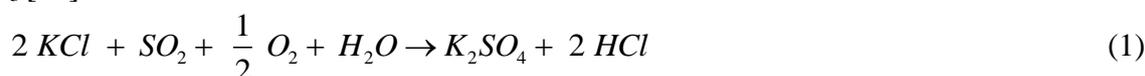
Fig. 5: Effect of sintering time on adhesion strength. KCl-K₂SO₄ (50 wt%) deposit, sintered at 650 °C, measured at 600 °C, steels pre-oxidized for 24 hours, 4 data points (24 for 4 hours).

3.3. Effect of composition

In order to study the effect of different components constituting typical biomass ashes, model fly ash compounds were prepared containing KCl, K₂SO₄, CaO, CaSO₄, SiO₂ and K₂CO₃. Since KCl and K₂SO₄ are the major species found in the inner layer of typical biomass ash deposits [14], the effect of CaO, CaSO₄, SiO₂ and K₂CO₃ was studied in the presence of KCl and K₂SO₄, with all the 3 components present in equal proportions.

The results highlight the effect of sulphates on adhesion strength, as seen in Fig. 6. The deposit containing KCl and K₂SO₄ (50 wt%) exhibited much higher adhesion strength compared to a deposit containing pure KCl. Similarly, the deposit containing KCl, K₂SO₄ and CaSO₄ (33 wt% each) showed higher adhesion strengths than KCl, K₂SO₄ and CaO. In boilers, KCl can undergo sulphation in the gas phase prior to deposition [15], or in solid phase after deposition on boiler surfaces [16]. While gas phase sulphation is faster than solid phase sulphation, the deposit is exposed to the flue gas for a longer period of time [16], making both sulphation mechanisms relevant.

Sulphation of KCl in deposits can occur as a gas-solid or gas-liquid reaction by SO₂ [17] or SO₃ [18].



These results provide substantial evidence that gas phase sulphation may result in an increase in adhesion strength at the investigated conditions. However, these results are not conclusive for solid phase sulphation. Further investigation of solid phase sulphation is required to completely understand the influence of the overall sulphation process on deposit adhesion strength. Nevertheless, it is speculated that reactions occurring between the deposit and the flue gas may be a cause of any adhesion strength variations observed in boilers.

Furthermore, the results portray the effect of SiO₂ and K₂CO₃. While Si is widely present in biomass ash deposits, the presence of K₂CO₃ has been identified in a few studies in literature [19, 20]. SiO₂ does not seem to significantly affect the adhesion strength under the conditions examined. However, the presence of K₂CO₃ considerably increases the adhesion strength. This is possibly due to the formation of Fe/Cr compounds originating from the reaction between K₂CO₃ and the steel.

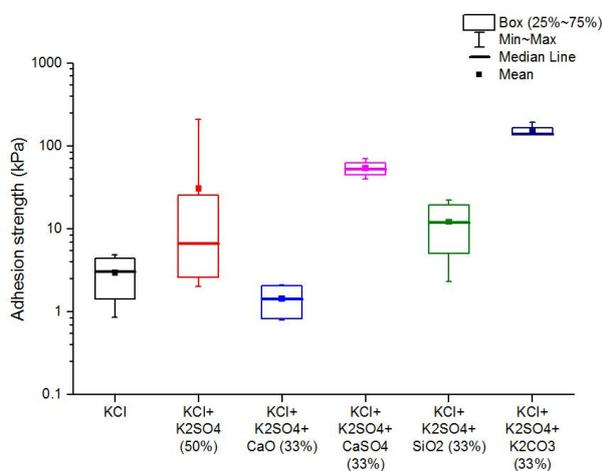


Fig. 6: Effect of composition on adhesion strength using model fly ash compounds. Deposits sintered at 650 °C (KCl+ K₂SO₄+ K₂CO₃ sintered at 600 °C) for 4 hours, measured at 600 °C, steels pre-oxidized for 24 hours, 4 data points (24 for KCl+K₂SO₄)

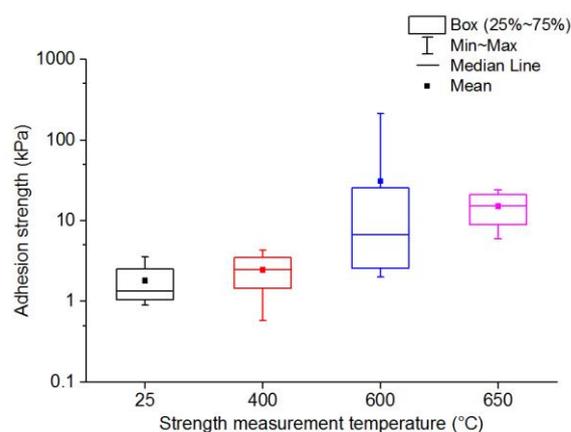


Fig. 7: Effect of strength measurement temperature on adhesion strength. KCl-K₂SO₄ (50 wt%) deposit, sintered at 650 °C for 4 h, steels pre-oxidized for 24 h, 4 data points (24 for 600 °C)

3.4. Effect of cooling down the deposit

Application of thermal shocks to induce deposit shedding is a technique commonly used to remove heavily sintered deposits from superheater tubes [3, 21]. This study further investigates the effect of thermal shocks by quantifying the effect of cooling down the deposit after sintering.

After sintering for 4 hours, the deposits were allowed to cool down to a specified temperature, prior to strength measurements. As seen in Fig. 7, cooling down the deposits results in a decrease in adhesion strength. Thermal stresses are induced at the deposit-tube interface, owing to differences in the thermal expansion coefficients between the deposit/corrosion layer and the steel tube [21]. As the result, cracks may develop at the interface, leading a decrease in the adhesion strength.

3.5. Analysis of the scatter in data

In order to better understand the significant scatter observed in the data, several experiments were conducted using KCl-K₂SO₄ (50 wt%) deposits. The experiments reveal that the adhesion strength data roughly follows a log-normal distribution, as seen in Fig. 8. This is similar to observations made using deposits from kraft recovery boilers [22]. Moreover, experiments conducted in biomass-fired full-scale boilers indicate similar trends [23].

The stochastic nature of debonding has significant implications on deposit shedding in boilers. The results suggest that even though soot-blowing may remove the majority of the deposits, the strongly adherent deposits might not be removed. Subsequent accumulation of strong deposits probably results in the eventual fouling of boiler surfaces [22].

However, the data obtained from the experiments may be used to optimize soot-blowing in boilers. As seen in Fig. 9, the probability of debonding of an ash deposit increases with increasing pressure applied. These results may be extended to incorporate changes in ash composition, temperature, steel type, sintering time, sulphation degree, etc., to predict optimal soot-blowing pressures for deposit shedding and suggest soot-blowing frequencies.

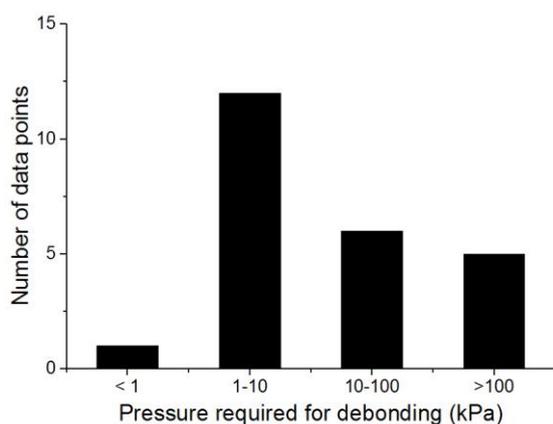


Fig. 8: Log-normal distribution of adhesion strength data. KCl-K₂SO₄ (50 wt%) deposit, sintered at 650 °C for 4 hours, measured at 600 °C, steels pre-oxidized for 24 hours, 24 data points

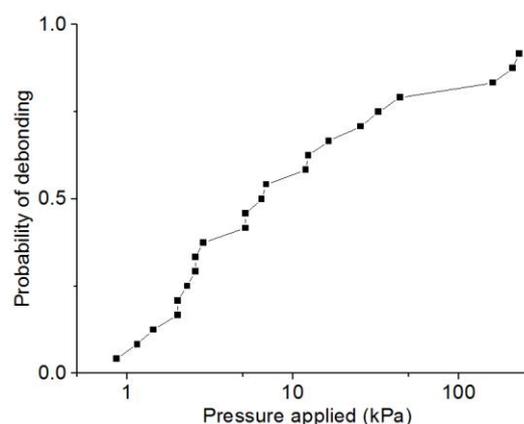


Fig. 9: Probability of deposit debonding vs pressure applied. KCl-K₂SO₄ (50 wt%) deposit, sintered at 650 °C for 4 hours, measured at 600 °C, steels pre-oxidized for 24 hours, 24 data points

4. Conclusions

This study investigated the shear adhesion strength of biomass ash deposits to superheater tubes. Increasing sintering temperatures resulted in greater adhesion strengths, with a sharp increase observed near the ash softening temperature.

Corrosion occurring at the deposit-tube interface leads to formation of a partially molten layer, resulting in increased adhesion strengths. Additionally, higher melt fractions at the interface leads to increased adhesion strength.

Sintering time did not significantly affect adhesion strengths up to 24 hours at the conditions investigated. However, deposits containing sulphates showed increased adhesion strengths, indicating that gas phase sulphation may result in the formation of stronger deposits. Additionally, the presence of alkali carbonates in the ash deposit significantly increased the adhesion strength at the investigated conditions.

Furthermore, it was substantiated that cooling down the deposit after sintering reduces the adhesion strength, due to thermal stresses induced at the deposit-tube interface. Finally, experiments revealed that adhesion strength data roughly follows a log-normal distribution.

The results allow better understanding of the process of deposit shedding, both qualitatively and quantitatively. Furthermore, the obtained data may be used to develop a tool for analyzing the effect of fuel composition on adhesion strength, and suggesting boiler operating conditions to prevent the formation of strong deposits. Additionally, the obtained data may be used to optimize soot-blowing in boilers.

5. Future work

Further experiments are being conducted to analyze the effect of steel type, ash particle size, and other model fly ash compounds. Additionally, experiments are being conducted with online solid phase sulphation of ash deposits to further investigate if solid phase sulphation of ash deposits results in a variation in adhesion strength. Furthermore, a setup is being constructed to determine the tensile strength of ash deposits. This setup incorporates temperature gradients across the deposit layer for superior replication of boiler conditions. Finally, a model is being constructed to optimize soot-blowing in boilers.

Acknowledgements

This work is part of the project, 'Flexible use of Biomass on PF fired power plants' funded by Energinet.dk through the ForskEL programme, DONG Energy and DTU.

References

- [1] ZBOGAR, A., FRANDBSEN, F., JENSEN, P.A. and GLARBORG, P. Shedding of Ash Deposits. *Progress in Energy and Combustion Science*, 2009, vol. 35, no. 1. pp. 31-56
- [2] OKORO, S.C., MONTGOMERY, M., FRANDBSEN, F.J. and PANTLEON, K. High Temperature Corrosion Under Laboratory Conditions Simulating Biomass-Firing: A Comprehensive Characterization of Corrosion Products. *Energy & Fuels*, 2014, vol. 28, no. 10. pp. 6447-6458
- [3] FRANDBSEN, F. *Ash Formation, Deposition and Corrosion when Utilizing Straw for Heat and Power Production*. Technical University of Denmark, Department of Chemical and Biochemical Engineering, 2010, ISBN- 9788792481405
- [4] European Standards on Solid Biofuels. *Method for the Determination of Ash Melting Behaviour*.
- [5] SUI, J., LEHMUSTO, J., BERGELIN, M. and HUPA, M. The Onset of Potassium Chloride Induced High Temperature Corrosion: A Novel Experimental Approach. *Oxidation of Metals*, 2014, vol. 82, no. 5-6. pp. 437-456

- [6] SHINATA, Y. and NISHI, Y. NaCl-Induced Accelerated Oxidation of Chromium. *Oxidation of Metals*, 1986, vol. 26, no. 3-4. pp. 201-212
- [7] PETTERSSON, J., ASTEMAN, H., SVENSSON, J. and JOHANSSON, L. KCl Induced Corrosion of a 304-Type Austenitic Stainless Steel at 600 C; the Role of Potassium. *Oxidation of Metals*, 2005, vol. 64, no. 1-2. pp. 23-41
- [8] SPIEGEL, M. Salt Melt Induced Corrosion of Metallic Materials in Waste Incineration Plants. *Materials and Corrosion*, 1999, vol. 50, no. 7. pp. 373-393
- [9] LEE, S. Corrosion, 47,(1991): P. 868 2, AS Kim and MJ McNallan, Corrosion, 46,(1990): P. 746 3, FH Stoot, R, Prescott, P. Elliott and M. H, JH A1'Atia, 6,(1988): P. 115 4, YY Lee and MJ McNallan. *Met.Trans.A*, 1987, vol. 18. pp. 1099
- [10] NIELSEN, H.P., FRANDSEN, F.J. and DAM-JOHANSEN, K. Lab-Scale Investigations of High-Temperature Corrosion Phenomena in Straw-Fired Boilers. *Energy & Fuels*, 1999, vol. 13, no. 6. pp. 1114-1121
- [11] PACKHAM, D.E. Handbook of Adhesion Technology, Springer, 2011 *Theories of Fundamental Adhesion*, pp. 9-38
- [12] KARLSSON, S., et al. Mitigation of Fireside Corrosion of Stainless Steel in Power Plants: A Laboratory Study of the Influences of SO₂ and KCl on Initial Stages of Corrosion. *Energy & Fuels*, 2014, vol. 28, no. 5. pp. 3102-3109
- [13] HURLEY, J.P., BENSON, S.A. and MEHTA, A.K. Ash Deposition at Low Temperatures in Boilers Burning High-Calcium Coals. *The Impact of Ash Deposition on Coal Fired Plants*, Washington: Taylor and Francis, 1994. pp. 19-30
- [14] JENSEN, P.A., et al. SEM Investigation of Superheater Deposits from Biomass-Fired Boilers. *Energy & Fuels*, 2004, vol. 18, no. 2. pp. 378-384
- [15] IISA, K., LU, Y. and SALMENOJA, K. Sulfation of Potassium Chloride at Combustion Conditions. *Energy & Fuels*, 1999, vol. 13, no. 6. pp. 1184-1190
- [16] SENDELØV, L.W., et al. Sulfation of Condensed Potassium Chloride by SO₂. *Energy & Fuels*, 2013, vol. 27, no. 6. pp. 3283-3289
- [17] HENRIKSSON, M. and WARNQVIST, B. Kinetics of Formation of HCl (g) by the Reaction between NaCl (s) and SO₂, O₂, and H₂O (g). *Industrial & Engineering Chemistry Process Design and Development*, 1979, vol. 18, no. 2. pp. 249-254
- [18] FIELDER, W., STEARNS, C. and KOHL, F. Reactions of NaCl with Gaseous SO₃, SO₂, and O₂. *Journal of the Electrochemical Society*, 1984, vol. 131, no. 10. pp. 2414-2417
- [19] WU, H., et al. Impact of Coal Fly Ash Addition on Ash Transformation and Deposition in a Full-Scale Wood Suspension-Firing Boiler. *Fuel*, 2013, vol. 113. pp. 632-643
- [20] BLOMBERG, T. Which are the Right Test Conditions for the Simulation of High Temperature Alkali Corrosion in Biomass Combustion?. *Materials and Corrosion*, 2006, vol. 57, no. 2. pp. 170-175
- [21] RAASK, E. *Mineral Impurities in Coal Combustion: Behavior, Problems, and Remedial Measures*. Taylor & Francis, 1985
- [22] KALIAZINE, A., CORMACK, D., EBRAHIMI-SABET, A. and TRAN, H. The Mechanics of Deposit Removal in Kraft Recovery Boilers. *Journal of Pulp and Paper Science*, 1999, vol. 25, no. 12. pp. 418-424
- [23] BASHIR, M.S., et al. Suspension-Firing of Biomass. Part 2: Boiler Measurements of Ash Deposit Shedding. *Energy and Fuels*, 2012, vol. 26, no. 8. pp. 5241-5255