Theoretical Analysis of Acid Dew Point Temperature and Vapour Condensation Characteristics of the Flue Gas

Ning Wang¹, Xuemin Liu², Jian Guan², Guoli Qi², Jianfei Zhang¹, Zhiguo Qu¹,*

¹MOE Key Laboratory of Thermo-Fluid Science and Engineering, School of Energy and Power Engineering, Xi’an Jiaotong University, Xi’an, Shaanxi 710049, PR China
²China Special Equipment Inspection and Research Institute, Beijing 100029, PR China
*Corresponding author’s e-mail: zgqu@mail.xjtu.edu.cn

Abstract. Based on the gas-liquid phase equilibrium and multi-component diffusion theory, an analytical model for predicting acid dew point temperature and vapour condensation characteristics of flue gas was developed. The effects of components content, ash particle radius, wall temperature, coal-burned type and excess air ratio have been investigated. The results indicated that the acid dew point temperature and vapour condensation rate will increase with both water and sulfuric acid vapour contents increase. Vapours are not prone to condense on the ash particles when the particle radius is less than the corresponding critical condensing radius. The vapour condensation characteristics can be divided into two different stages with the wall temperature varies. The particle radius has a significant influence on the vapour condensation characteristics in the higher temperature stage. The acid dew point temperatures present significant differences for different coal-burned types, and the water vapour condensation rate is more sensitive to excess air ratio compared with the acid condensation rate.

1. Introduction
During the last several years, the waste heat recovery has received extensive attention in achieving energy highly efficient utilization and pollution emission reduction of the industrial systems. As an important industrial waste heat resources, the different temperature and component flue gas is basically utilized by the heat exchangers, such as air preheaters and economizers. However, the severe challenge of the flue gas utilization is the presence of SO₂ and ash particles at the coal-burned boilers. The sulfuric acid vapour increases the ADP (acid dew point), which significantly causes the heat exchanger corrosion, resulting in ash blocking, combustion deterioration and operating unsafety of the system [1]. Previous studies have shown that the low temperature corrosion is not only affected by the ADP, but also related to the acid vapour condensation characteristics [2].

Several scholars [3-4] have corrected several empirical or semi-empirical formulas by the experimental data combined with thermodynamic theory to predict the ADP. In order to improve the accuracy and application range of the model, more in-depth researches were conducted recently. ZareNezhad and Aminian [5] adopted a three-layer feedforward artificial neural network intelligent algorithm to establish an accurate ADP model of flue gas under multi-parameter variables, which can be applied to low temperature corrosion prevention and waste heat recovery. Wang et al [6] developed a numerical model to compare the ADP distributions of H-type, dimple, vortex generators and composite fin structures in economizers of the boiler, the effect of ash particle size was also discussed.
With respect to the prediction of vapour condensation characteristics, Yin et al [7] established a water vapour laminar film condensation with a small amount of oxygen (0%-3%) in a three-dimensional microchannel by the VOF (volume of fluid) method. It is worth noting most of the current studies considered the water vapour condensation characteristics, but there are only few researches focused on multi-component vapour condensation in flue gas. Wilson [8] revised the mathematical model of the component partial pressure on the gas-liquid interface of sulfuric acid solution, and proposed the calculation method of the sulfuric acid and water vapour condensation rate. Jin et al. [9] numerically explored the acid condensation rate in the chimney based on the above method. The result can be implemented to predict the life and design anti-corrosion configuration of the chimney.

In this paper, an analytical prediction model is developed to investigate the various parameter effect on the ADP and vapour condensation characteristics, such as flue gas component content, ash particle radius, wall temperature, coal-burned type and excess air coefficient. This work can provide guidance for the prevention of low temperature corrosion on the heat transfer surface in the flue gas.

2. Methodology

2.1 Mathematical model

In this section, the gas-liquid phase equilibrium and multi-component diffusion theory are introduced to establish the analysed model. The ADP and vapour condensation characteristics on the heat transfer wall and ash particles are compared respectively. The following assumptions are made: Thermal resistance of the condensate film is neglected; Flue gas should be considered as ideal mixture gas; Coal should be considered completely burned and the ash particles in the flue gas are spherical.

The flue gas composition after complete combustion can be determined by the combustible elements in the fuel. The required theoretical air amount and SO2 volume can be expressed as:

\[ V^0 = 0.0889(C_{as} + 0.375S_{as}) + 0.265H_{as} - 0.0333O_{as}, \quad V_{so2} = 0.7S_{as} / 100 \]

Only little SO2 is oxidized to SO3 in the flue gas, the SO2 is further reacted with H2O to form sulfuric acid vapour. The conversion percent of SO3 is depended on the flue gas temperature (Figure 1). CO2, N2 and H2O volume after complete combustion:

\[ V_{co2} = 1.866C_{as} / 100, \quad V_{N2} = 0.79V^0 + 0.8N_{as} / 100, \quad V_{H2O}^0 = 11.1H_{as} / 100 + 1.24M_{as} / 100 + 0.016V^0 \]

The actual flue gas volume can be calculated as:

\[ V_g = V^0 + (\alpha - 1)V^0 + 0.016I(\alpha - 1)V^0 \]

where \( C_{as}, S_{as}, H_{as}, O_{as} \) and \( N_{as} \) denote the content of carbon, sulfur, hydrogen, oxygen and nitrogen.

The component partial pressure on the gas-liquid interface of sulfuric acid solution can be obtained based on the gas-liquid phase equilibrium theory [8]:

\[ \ln p_i = a_iA + b_iB + c_iC + \Delta H_i^vD + \Delta S_i^vE + \frac{\Delta M_i}{F} + \frac{\Delta L_i}{G} + \alpha_iH + \ln \phi_i \]

where the A-H is the coefficient, which is only related to the temperature; i represents different components; \( a_i, b_i, c_i, \Delta H_i^v, \Delta S_i^v \) are pure component thermodynamic parameters; the others are component dependent parameters. These can be found by reference [8].

Part of the sulfuric acid solution will be decomposed into water and SO3 vapour. It is necessary to correct the partial pressure of each component by the apparent fugacity coefficient:

\[ p_{so2} = p_i / \phi_{so2}, \quad \phi_{so2} = p_w / [p_w + K_0 + K_1(p_w)^2], \quad \phi_{so2} = 1/[1 + K_1p_w] \]

where \( \phi_{so2} \) and \( \phi_{w0} \) are the apparent fugacity correction coefficients of sulfuric acid and water vapor; \( K_0 \) and \( K_1 \) are reaction equilibrium constants.
When the sulfuric acid vapor condenses on the heat transfer surface, the vapor needs to pass through the other vapors. The vapor mass transfer rate can be expressed as [10]:

\[ m_i = -\rho D_{\text{eff}} \nabla y_i, \quad D_{\text{eff}} = (1-x_i) \sum_{j=1}^{n} \frac{x_j}{D_{ij}} \quad D_{ij} = \frac{0.010471^{1.75} (1/M_i + 1/M_j)^{0.5}}{P(y_i^{1/3} + y_j^{1/3})^2} \]

The relationship between the two condensation rates is as below:

\[ X_a = R_a / (R_a + R_w) \]

where \( X_a \) is the sulfuric acid solution molar concentration; \( R_a \) and \( R_w \) are the mass transfer rates of sulfuric acid and water vapor.

The surface curvature of the ash particles increases the component partial pressure at the gas-liquid phase interface of the sulfuric acid solution, which can be corrected as the below [10]:

\[ p_{a,i} = p_{a,i}^* \exp(2\sigma M / \rho R T_p) \]

Based on the above mathematical model, the ADP and vapour condensate characteristics of flue gas under different parameters can be determined by the iterative method (Figure 2).

![Figure 1. Sulfuric acid vapor conversion percent](image)

![Figure 2. Iterative flow chart](image)

2.2 Model validation

During the iterative process, the accurate prediction of the vapour partial pressure on the gas-liquid interface of the sulfuric acid solution is strongly determined to the accuracy of the whole model. Therefore, it is necessary to verify the water and sulfuric acid vapour partial pressure. The water and sulfuric acid vapour partial pressure on the gas-liquid interface at different temperatures and solution concentration were compared with the experimental data [8], as shown in Figure 3. It can be seen that the experimental data and the calculation results show good consistency.
3. Results and Discussion

3.1 Effect of vapour contents

The vapour condensation characteristics of the flue gas are mainly influenced by the water and sulfuric acid vapour contents. Generally, the water and sulfuric acid vapour contents in the flue gas of coal-burned boilers are 5-50 ppm and 5%-16%, respectively. Figure 4 presents the effect of vapour contents on ADP of the wall and ash particles (0.1 μm). It can be seen that as the water or sulfuric acid vapour contents increase, the ADP gradually increases, while the corresponding increasing rate gradually decreases, which means the higher vapour contents have a less effect on the ADP. When the sulfuric acid vapour content increases from 5 ppm to 50 ppm, the ADP of the heat transfer wall and the ash particles can be increased by 18.85% and 18.89%. Additionally, when the water vapour content increases from 5% to 16%, both ADPs are increased by 7.36% and 7.61%, indicating that the ADP is more susceptible to the sulfuric acid vapour content. Moreover, the ADP of the ash particles is always lower than the ADP of heat transfer wall under the same conditions, it means the surface of the ash particles is more difficult to condense, which is caused by the increase of the component partial pressure due to the curvature of the particles.

![Figure 4. ADP variations with the vapor contents](image)

(a) Sulfuric vapour content
(b) Water vapour content

Figure 5 shows the effect of vapour contents on condensation characteristics. It can be found that the water and sulfuric acid vapour condensation rates increase linearly with the sulfuric acid vapour increases under the constant water vapour content. The sulfuric acid vapour condensation rate increases more quickly. Remarkably, the vapour content has little effect on the sulfuric solution concentration. As shown in Figure 5(b), when the sulfuric acid vapour content in the flue gas is constant, both the two vapour condensation rates show an increasing trend. The influence of water vapour content in the flue gas on the condensation rate is relatively weaker compared with the sulfuric acid vapour. Moreover, the condensation rate on the ash particles is smaller than the heat transfer wall under the same conditions. However, the vapour condensation rate on the particle surface gradually approaches the value of the heat transfer wall with the increase of water vapour content, indicating that the effect of ash particles on the condensation rate is weaker in the case of high water vapour content. On the other hand, unlike the influence of the above-mentioned sulfuric acid vapour, an increasing water vapour content causes a sharp drop in the sulfuric acid solution concentration.
3.2 Effect of heat transfer wall temperature
The heat transfer wall temperature is the main factor affecting the vapour condensation characteristics under the constant vapour contents. Figure 6 shows the vapour condensation rate variation curves with the heat transfer wall temperature. The curves can be divided into two different stages. When the wall temperature is varied from 50 °C to 110 °C (Stage 1), the water vapour condensation rate drops sharply and then begins to decrease slowly, while the sulfuric acid vapour condensation rates are increased linearly by 31.66% in this stage. As the wall temperature increases (Stage 2), the water vapour condensation rates continue to decrease quickly and start to separate, while the corresponding sulfuric acid vapour condensation rate begins to decrease sharply until the condensation disappears.

Additionally, as the wall temperature increases, an increasing trend is presented for the sulfuric acid solution concentration. It is also worth noting that the high temperature wall has a significant influence on the vapour condensation characteristics of the fly ash particles. At the first stage, when the wall temperature is relatively low, the vapour condensation rate of the different fly ash particle radius under the same input parameters is almost constant. As the wall temperature continues to rise, the curves of the vapour condensation rate of the different fly ash particles radius begin to separate. The smaller of the fly ash particles radius, the lower the corresponding condensation rate at the same temperature, the lower the corresponding ADP.

3.3 Effect of coal-burned type and excess air ratio
The composition contents of the flue gas are mainly determined by the coal-burned type and excess air coefficient. In this section, five common coal-burned types are considered, which are divided into 10 specific coal-burned groups. Figure 7 shows that the ADP variations for different coal types, the temperature difference of the ADP corresponding to the wall surface and the fly ash particles for all coal-burned types is nearly constant, which are about 3.6 °C. The ADP of the different coal-burned type flue gas are significantly different, the maximum temperature difference is about 30 °C.
Figure 8. Effect of excess air ratio on vapour condensation characteristics

Figure 8 shows the effect of excess air ratio on the vapour condensation rate. As the excess air ratio increases from 1.05 to 1.5, the water and sulfuric acid vapour condensation rate decreases correspondingly, and the decreasing speed gradually becomes slower. Moreover, the water vapour condensation rate variation under the same coal-burned type is larger than the sulfuric acid vapour. For example, the sulfuric acid vapour condensation rate of the group 2 is reduced by 32.61%, but the corresponding water vapour condensation rate is decreased by 40.23%, indicating that the water vapour condensation rate is more sensitive to the changes of the excess air ratio.

4. Conclusions

Based on the gas-liquid phase equilibrium and multi-component diffusion theory, a theoretical model about ADP and vapour condensation characteristics of flue gas is developed. The effects of different parameters are discussed. The main conclusions are as follows:

(1) The ADP of the flue gas gradually increases with the water or sulfuric acid vapour content increases, and the ADP is more susceptible to the sulfuric acid vapour content. The ADP of the ash particles is always lower than the ADP of the heat transfer wall under the same conditions, it means the surface of the ash particles is more difficult to condense.

(2) The vapour condensation characteristics can be divided into two different stages according to the wall temperature variation, the high wall temperature has an obvious influence on the vapour condensation rate of the fly ash particles.

(3) The ADP corresponds to different coal-burned types coal are different completely, the water vapour condensation rate is more sensitive to the excess air coefficient than the sulfuric acid vapour.

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