Prediction of flue gas acid dew point temperature distribution range in boilers

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Abstract. Prediction of the acid dew point temperature of flue gas has a great effect on the heat exchangers design or control as recover energy from the boiler exhaust gas. The present study focuses on the prediction of the flue gas acid dew point temperature as well as its distribution interval, which can further help to prevent and resist the low temperature corrosion from the flue gas. Popular prediction models of acid dew point are reviewed. The 1973 version of Soviet Union calculation standard model has a priority to calculate the mean acid dew point prediction in coal fired boilers, and the Okkes model is also recommended for different types of boilers. Several groups of experimental and published data are substituted to different prediction models for analysis, and the results show that the Verhoff & Banchero model and Haase & Borgmann model can be explored to calculate the upper and lower limits of the distribution interval of the acid dew point.

1. Introduction

The direct feature of boiler convective exchangers, such as economizer and air pre-heater, is to reduce the temperature of the exhaust gas for energy recovery [1-3]. Generally, a 10-15 °C temperature drop of boiler exhaust gas can lead to an increase of boiler thermal efficiency by 1% [4]. However, it is impossible to install too many exchangers for a perfect energy saving, because that the acid gas in the flue gas together with water vapor will generate liquid acid when the flue gas temperature is cooled by the exchanger below the acid dew point temperature (tADP), and then the liquid acid will further result in a corrosion on the surface of the heat exchanger, which is called Low Temperature Corrosion (LTC) and directly leads to serious decrease in the heat exchangers safety and life [5-7]. Therefore, the surface temperature of exchangers should be controlled higher than the tADP to avoid LTC [8].

The tADP of the boiler flue gas cannot be obtained easily since the gas components are too much complex and changeable, and thus the tADP often depends on the experimental data as well as theirs fitting curve formula and empirical prediction models [9-16]. The experimental test in the present study is called direct method, and the tADP form prediction model is called indirect method. For direct method, its test system is often complicated because of the changeable gas components, fly ash, water vapor condensation, sensor precision, etc., which often make the experimental system overpriced. Instead, developing indirect method will need less consumption due to the existing thermodynamics theory and experimental data. For decades of studies, there are dozens of empirical or semi-empirical formulas have been proposed to predict the tADP, and these methods can be divided into two categories: (1) the tADP is derived from the fuel composition [8, 9, 17-18], and (2) the tADP is predicted from the gas
contents of SO3/So2 and H2O in the combustion products [10-16]. In recent years, the development of numerical simulation also creates numerical methods to predict the $T_{ADP}$ with high prediction accuracy, such as CFD simulations [2, 19-21] and numerical iterations [1, 3, 7, 22]. However, these studies almost focus on the mean $t_{ADP}$, while few have paid attention to the $t_{ADP}$ distribution range. As described in ref. [23], the $t_{ADP}$ always varies in an interval with about 30-60 °C width at a certain SO3 content. For this phenomenon, we can conclude that good temperature control of exchangers against LTC not only needs an accuracy prediction of mean $t_{ADP}$ but also its distribution range.

In the present study, we focus on both the $t_{ADP}$ and its distribution range predictions on the basis of the indirect methods. We choose three groups of tested data from operating boilers to predict $t_{ADP}$ and its distribution range for analysis, and some published data are also employed for the comparison. From the analysis, we shall recommend effective $t_{ADP}$ prediction methods for a further control of the boiler exchanger temperature.

2. Review on acid dew point prediction models

2.1 Prediction models derived from fuel composition

The Soviet Thermodynamic Calculation Standard (1973 edition) formula (here we called it as Soviet Standard Model 1973) [9] is one of the most classic models to calculated $t_{ADP}$, expressed by,

$$
t_{ADP} = \beta \sqrt[3]{S^\Pi} \frac{1}{1.05^{a_{ash}A^\Pi}} + t_{DP} \tag{1}
$$

where $t_{DP}$ (°C) is the dew point temperature of the water vapor in the boiler exhaust gas, $S^\Pi$ and $A^\Pi$ the equivalent sulfur content and ash content (% mass percentage), respectively, $a_{ash}$ the fly ash coefficient, and $\beta$ the empirical coefficient which often equals to 125. The $t_{DP}$ can be obtain from the saturated water vapor thermal properties with its partial pressure ($p_{H2O}$, Pa), or predicted by fitting formula, here we shall provide a simple equation cited from ref. [24], given by,

$$
t_{DP} = 42.4332(p_{H2O})^{0.13434} - 100.35 \tag{2}
$$

The parameters of $S^\Pi$ and $A^\Pi$ are converted according to the sulfur content $S_{ar}$ and ash content $A_{ar}$ as received basis (% mass percentage), expressed by,

$$
S^\Pi = 4187S_{ar} / Q_{ar,net}, \quad A^\Pi = 4187A_{ar} / Q_{ar,net} \tag{3}
$$

where $Q_{ar,net}$ is the fuel net calorific value as received basis, kJ/kg. The last parameter $a_{ash}$ denotes the ratio of the fly ash mass to the total ash mass in the combustion products, and one can obtain $a_{ash}$ by experimental test. In addition, we shall introduce some empirical data of coal fired boilers for reference, which are recommended from Ref. [4], as shown in Table 1.

| Combustion mode                  | $a_{ash}$ |
|----------------------------------|-----------|
| Inclined reciprocating grate     | 0.1 − 0.2 |
| Travelling grate stoker          | 0.1 − 0.2 |
| Spreader stoker                  | 0.2 − 0.3 |
| Circulating fluidized bed        | 0.4 − 0.5 |
| Pulverized coal fired boiler      | 0.8 − 0.9 |
| Coal-water slurry                | 0.7 − 0.8 |

Some notes of the Soviet Standard Model 1973 are as follows: (1) it is mostly used to predict the coal fired boilers as well as solid fuel fired boilers, but for oil-fired boiler it sometimes presents underestimated predictions [23], (2) For high percentage of alkaline oxide in the ash and $A_{ar} > 35\%$, Eq.
(1) may overestimate the $t_{ADP}$ [9], (3) it is not recommended when $S^{II} < 0.2$ [25], (4) once the desulfurization measures are carried out during the boiler operation, Eq. (1) should be modified by the SO$_3$ desulfurization rate ($\eta_{SO_3}$), i.e. replace $S^{II}$ in Eq. (1) with $S^{II}(1-\eta_{SO_3})$ [26], and (5) it can be used without boiler running, and thus is mostly selected for the design of boiler as well as its exchangers. There are also some modified models based on Eq. (1) for special cases, in which good predictions cannot be obtained from Eq. (1). Li et al. replace the following formula expressed by [18]

$$t_{ADP} = \frac{1.1\beta \sqrt[10]{S^{II}}}{1.05} + t_{DP}$$

(4)
to deal with the underestimated prediction from Eq. (1). To consider the effect of alkaline oxide in the ash, A.Ф Гаврцлов also proposed a modified model, given by [23, 25],

$$t_{ADP} = \frac{\beta \sqrt[10]{S^{II}}}{K} + t_{DP}$$

(5)
where $K$ is ash characteristic coefficient as the functions of CaO & MgO mass contents compared to the total ash mass. In addition, a simple empirical formula, expressed by,

$$t_{ADP} = 120 + 17(S^{II} - 0.25), \quad S^{II} > 0.25$$

(6)
is describe in Ref. [8], which is a rough prediction model with low accuracy. This model is often used to quickly estimate the magnitude of the $t_{ADP}$ under the condition that the ash content $A_{ash}$ is unknown.

### 2.2 Prediction models derived from exhaust gas contents

The prediction model derived from exhaust gas contents is simpler than that from fuel composition. Once the components of gaseous SO$_2$/SO$_3$ and H$_2$O are measured, the results can be fast obtained. Since the predictions need the components of the combustion products, the experimental test must combine with the boiler running, therefore, the second kind model is mostly selected for the temperature control of the boiler exchangers. The widely used models are listed in Table 2.

| Model          | Expression                                      | Dimension | Index |
|----------------|-------------------------------------------------|-----------|-------|
| Muller Model [10] | $t_{ADP} = 116.55 + 16.06 \log V_{SO_2} + 1.05(\log V_{SO_3})^2$ | V, ppm    | Eq. (7) |
| Halstead Model [11] | $t_{ADP} = 113.02 + 15.08 \log V_{H_2SO_4} + 2.10(\log V_{H_2SO_3})^2$ | V, ppm    | Eq. (8) |
| Okkes Model [12] (Version A) | $t_{ADP} = 10.88 + 27.6 \log p_{H_2O} + 10.83 \log p_{SO_2}$ | p, Pa     | Eq.(9a) |
|                  | $+ 1.06(\log p_{SO_3} + 2.9943)^{19}$            |           |       |
| Okkes Model [12] (Version B) | $t_{ADP} = 203.25 + 27.6 \log p_{H_2O} + 10.83 \log p_{SO_2}$ | p, atm    | Eq.(9b) |
|                  | $+ 1.06(\log p_{SO_3} + 8)^{19}$                |           |       |
| Verhoff & Bancher [13] (Version A) | $\frac{1000}{t_{ADP} + 273.15} = 1.784 + 0.027 \log p_{H_2O} - 0.103 \log p_{SO_2}$ | p, atm    | Eq.(10a) |
|                  | $+ 0.034 \log p_{H_2O} \log p_{SO_2}$           |           |       |
| Verhoff & Bancher [13] (Version B) | $\frac{1000}{t_{ADP} + 273.15} = 2.988 - 0.1376 \log p_{H_2O} - 0.267 \log p_{SO_2}$ | p, Pa     | Eq.(10b) |
|                  | $+ 0.03287 \log p_{H_2O} \log p_{SO_2}$         |           |       |
| Japan Power Model [14] | $t_{ADP} = 20 \log V_{SO_2} + a - 80$ | V, ppm    | Eq. (11) |

### Table 2 (cont.). Prediction models of $t_{ADP}$ (°C) derived from exhaust gas contents

| Model          | Expression | Dimension | Index |
|----------------|------------|-----------|-------|
| Muller Model [10] | $t_{ADP} = 116.55 + 16.06 \log V_{SO_2} + 1.05(\log V_{SO_3})^2$ | V, ppm    | Eq. (7) |
| Halstead Model [11] | $t_{ADP} = 113.02 + 15.08 \log V_{H_2SO_4} + 2.10(\log V_{H_2SO_3})^2$ | V, ppm    | Eq. (8) |
| Okkes Model [12] (Version A) | $t_{ADP} = 10.88 + 27.6 \log p_{H_2O} + 10.83 \log p_{SO_2}$ | p, Pa     | Eq.(9a) |
|                  | $+ 1.06(\log p_{SO_3} + 2.9943)^{19}$            |           |       |
| Okkes Model [12] (Version B) | $t_{ADP} = 203.25 + 27.6 \log p_{H_2O} + 10.83 \log p_{SO_2}$ | p, atm    | Eq.(9b) |
|                  | $+ 1.06(\log p_{SO_3} + 8)^{19}$                |           |       |
| Verhoff & Bancher [13] (Version A) | $\frac{1000}{t_{ADP} + 273.15} = 1.784 + 0.027 \log p_{H_2O} - 0.103 \log p_{SO_2}$ | p, atm    | Eq.(10a) |
|                  | $+ 0.034 \log p_{H_2O} \log p_{SO_2}$           |           |       |
| Verhoff & Bancher [13] (Version B) | $\frac{1000}{t_{ADP} + 273.15} = 2.988 - 0.1376 \log p_{H_2O} - 0.267 \log p_{SO_2}$ | p, Pa     | Eq.(10b) |
|                  | $+ 0.03287 \log p_{H_2O} \log p_{SO_2}$         |           |       |
| Japan Power Model [14] | $t_{ADP} = 20 \log V_{SO_2} + a - 80$ | V, ppm    | Eq. (11) |
### 2.3 Calculation of SO$_3$ content

The volume content of SO$_3$ is too low (~1.0 ppm or ~10 ppm) to directly detect by the equipment of smoke analyzer. Therefore, the SO$_3$ content is often predicted from the SO$_2$ content which can be easily tested by apparatus. Zhang [23] proposed a fitting formula out of some published data to predict the conversion ratio of the SO$_2$ to the SO$_3$, expressed by,

\[ \begin{aligned}
V_{SO_3} &= K_{SO_3} V_{SO_2} \\
K_{SO_3} &= m(\alpha - 1) V_{exhaust} S_{ar}^{0.1}
\end{aligned} \]  

where $K_{SO_3}$ is the conversion ratio of (SO$_2$ $\to$ SO$_3$), $\alpha$ the excess air coefficient, $V_{exhaust}$ the volume of 1.0 kg exhaust gas (m$^3$/kg), and $m$ the coefficient dependent with $\alpha$. For pulverized coal combustion, $m = 1.0$ with $\alpha < 0.135$, and for $\alpha \geq 0.135$, $m = 0.143/(\alpha-1)$. For oil combustion, $m = 3.94$ with $\alpha < 0.135$, and for $\alpha \geq 0.135$, $m = 0.53/(\alpha-1)$.

Equation (15) is complicated to calculate, and we prefer to substitute the element balance of $V_{SO_3} = 0.007 S_{cal}$, where $S_{cal}$ denotes the calculating sulfur mass content and usually can be replaced by $S_{ar}$, into Eq. (15) for convenience, and then we have,

\[ K_{SO_3} = 0.007 m(\alpha - 1) S_{ar}^{0.9} / V_{SO_2} \]  

In Eq. (16), all the input parameters can be directly obtained, and thus significantly reduce the difficult of the calculations.

Although Eq. (15) is an explicit formula, the $m$ parameter is still insufficient to predict the $K_{SO_3}$ of other types of boilers, and thus we usually prefer the empirical value for the calculations. To simplify the predictions, we shall conclude a fast prediction method as follows: (1) the volume content of water vapor in the flue gas often distributes during 10–14%, and we can choose 12% for an average estimation [8, 15], (2) 500 ppm of SO$_2$ in the flue gas could be corresponding to 1% of $S_{ar}$, and this relation can be assumed as a linear relationship [8], i.e. $V_{SO_2} \approx 500 S_{ar}$, and (3) the value of $K_{SO_3}$ mostly distributes in the range of 0.5–3% (the Maximum is about 5%), and Blanco and Pena [27] used $K_{SO_3} = 1\%$ for calculation and obtained a good prediction curve as the $V_{SO_3} < 5$ ppm). Generally, $K_{SO_3} = 3\%$ would be enough to get safe predictions against the low temperature corrosion [8].

| Exponential Model | $t_{ADP} = t_{DP} + B \cdot (p_{H_2SO_4})^n$ |
|-------------------|-----------------------------------------------|
| Варанова Model [8, 15] | $t_{ADP} = 186 + 20 \log V_{H_2O} + 26 \log V_{SO_3}$ |
| Haase & Borgmann Model [16] | $t_{ADP} = 255 + 18.7 \log p_{H_2O} + 27.6 \log p_{SO_3}$ |

Remark:
1. Eq. (8) is based on $V_{H_2O} = 11\%$, for $V_{H_2O} < 9\%$ or $> 13\%$, $t_{ADP} = t_{ADP} - 3$ or $+3$ °C, respectively.
2. Calculations by Eqs. (9a) and (9b) are equal, and Eqs. (10a) and (10b) also have identical predictions.
3. In Eq. (11), $a = 184$, 194, 201 for water vapor contents $= 5\%$, $10\%$, $15\%$, respectively.
4. Eq. (12) includes two versions, named Version A and Version B for different parameters of $B$ and $n$, and details of the $B$ and $n$ are listed in Refs. [7, 23].
3. Result and discussion

3.1 Importance of acid dew point distribution range

During the boiler operation, once the exhaust gas flows across the tube banks of the exchangers, complicated flow field and temperature field may occur, such as boundary effect, backflow, vortex, fly ash effect, and these factors inevitably have significant effect on the SO$_2$/SO$_3$ and water vapor content, finally making the $t_{ADP}$ always change. Figure 1 shows the statistics of $t_{ADP}$ distribution for the coal fired boiler. From Fig.1, we can find that the $t_{ADP}$ generally varies in a special interval when the $V_{SO_3}$ is fixed, in which the upper limit is about 30-60 °C higher than the lower limit as the $V_{SO_3}$ > 10 ppm. For instance, when $V_{SO_3} = 20$ ppm, $t_{ADP}$ distributes between 70 and 110 °C, and for $V_{SO_3} = 40$ ppm, $t_{ADP}$ varies during 100 and 160 °C. In this study, we shall assume 50 °C as the average interval width.

Once the $t_{ADP}$ distribution range is obtained, the interval upper and lower limits will be two critical temperature points for the exchanger design and control. If the Minimum surface temperature of the exchanger is higher than the upper limit temperature, i.e. right zone of the shadow in Fig. 1, low temperature corrosion will not occur. Conversely, once the Maximum surface temperature of the exchanger is in the left zone of the shadow, the low temperature corrosion must emerge. If the surface temperature of the exchanger distributes in the shadow, we should take necessary protective measures against the low temperature corrosion.

![Fig. 1 Acid dew point distribution of the coal fired boilers. (The data are digitized from Ref. [23])]()

3.2 Prediction of acid dew point and its distribution range

Figure 2 shows the results predicted by the present experimental data which is tested from three operating boilers in the city of Xi’an. The types of the three boilers are DHL140-1.6/110/70-AII, QXL70-1.6/13/70-AII, and SHL20-13-A, of which the boiler capacity is 140MW (~200 t/h), 70MW (~100t/h), and 20 t/h (~14 MW). The tested boiler capacities cover two magnitudes, so that the test data would be more representative for the comparisons. The index number means: 1- Soviet Standard Model 1973, 2- Haase and Borgmann Model, 3- Baranowa Model, 4- Okkes Model, 5- Verhoff & Banchero Model, 6- Japan Power Model, 7- Exponential Model A, 8- Exponential Model B, 9- Muller Model, and 10- Halstead Model.

From Fig. 2, we can find most predictions distribute above the blue dash line (lower limit of the interval, corresponding to Haase & Borgmann Model) and below the wed dash line (upper limit of the interval, corresponding to Verhoff & Banchero Model), and the interval range width is not great than 50 °C, which denotes that the assumption in Sec. 3.1 is reasonable and can be effectively to predict the acid dew point and its distribution range. The predictions by Exponential Model A (index number = 7) are not in the $t_{ADP}$ distribution interval, while the calculation by Exponential Model A can meet the requirement.

For the comparison of the mean $t_{ADP}$ predictions (Note that, we choose $K_{SO_3} = 1.5\%$ for the prediction of SO$_3$ content. The exhaust gas pressure is fitted as 1.0 atm, and the water vapour content
is assumed 10% if it is not available by the equipment test), the Soviet Standard Model 1973 is firstly to be recommended for the designing calculation of the coal fired boiler. For controlling the temperature of the exchangers, most of the models listed in Table 2 (except Exponential Model A) can be used, and in the present study we shall recommend Okkes Model for the prioritized method since this formula is a modified model based on Muller Model, of which includes the water vapour effect and can be use for different types of boilers [18, 24-26].

![Diagram](image)

Fig.2 Comparison of \( t_{ADP} \) predictions among different models with the present test data.
(a) 140MW (~200t/h), (b) 70MW (~100t/h), (c) 20t/h (~14MW).

Figure 3 depicts the predictions of the \( t_{ADP} \) corresponding to the published data of a coal fired boiler [23], an oil fired boiler [23] and a circulating fluidized bed boiler [28], and the flue gas content of the fluidized bed boiler is artificially controlled with a fixed \( O_2 \) content, which is called artificial controlled flue gas in this study. The meanings of the number index are consistent with that in Fig. 2.

In Fig. 3, Haase & Borgmann Model and Verhoff & Banchero Model are used to evaluate the lower and upper limits of the \( t_{ADP} \) distribution interval. We can find that most of the predictions are in the distribution interval except two points, i.e. Point 7 in Fig. 3(b) and Point 1 in Fig. 3(c), and the two exceptions can be explained as follows, (1) the former is calculated with Exponential Model A which is not suitable for the prediction as proved in the Ref. [23, 26] and by the above examples, and (2) the latter is predicted by the Soviet Standard Model 1973 which is not recommended in the case of \( S^\alpha<0.2 \) as mentioned in Section 2.1 (here, the value of \( S^\alpha \) is about equal to 0.164, with an assumption of \( Q_{ar,net} = 20000 \text{ kJ/kg} \)). In addition, the \( t_{ADP} \) of point 1 in Fig. 3(b) is slightly lower than the lower limit, and this exception can be attributed to the liquid fuel, i.e. oil, of which the ash content is too low to use the Soviet Standard Model 1973 for calculations.
Fig. 3 Comparison of \( t_{ADP} \) predictions among different models with published data.

4. Conclusions
The prediction methods of the acid dew point temperature of the flue gas in boilers are studied, and the widely used prediction models are also reviewed. The existing models are mostly used to calculate the mean acid dew point instead of its distribution range. The present study focus on the prediction of the upper and lower limits of the changeable acid dew point, and the purpose is to further prevent and resist the low temperature corrosion of the exchangers. Six group data are introduced to predict the acid dew point for comparisons. The Soviet Standard Model 1973 is more suitable for the coal fired boilers on the condition of the equivalent sulfur content higher than 0.2%, and the Okkes model can be used for many types of boilers. The Soviet Standard Model 1973 is preferred for the designing calculation of the exchanger temperature, while the Okkes Model is recommended for the control of the exchanger temperature. The Verhoff & Banchero model and Haase & Borgmann model is recommended to calculate the upper and lower limits of the acid dew point distribution range, respectively.

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