Cause analysis and countermeasure of blockage in urea pyrolysis denitration system of coal-fired power plant

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Abstract. Due to the safety and convenience storage of raw materials and the maturing technology, the method of urea pyrolysis for ammonia has been widely used in the selective catalytic reduction (SCR) denitration technology of thermal power plants. However, crystallization and blockage phenomena occurred frequently, seriously disrupting the normal operation of SCR denitrification systems. In order to analyze the reasons of crystallization plugging in urea pyrolysis process, This paper collects and analyzes the scaling samples from pyrolysis furnace and spraying ammonia pipe to identify scaling substances, analyzes the reasons of urea crystallization, puts forward the improvement measures so as to guarantee the safety and steady operation of SCR-DeNOx system.

1. Introduction
Urea can be prepared by hydrolysis and pyrolysis methods to produce reducing agent ammonia. In comparison, the urea pyrolysis process has the advantages of simple system, fast reaction speed, safety and convenience, etc. However, the urea pyrolysis reaction process accompanied by complex physical and chemical reactions, including atomization, evaporation, precipitation, drying and decomposition processes. When urea is decomposed into ammonia gas, it also generates complex intermediate products due to incomplete reaction, which leads to crystallization and precipitation. With the accumulation of sediments, the urea pyrolysis system often appears crystallization blockage phenomenon in pyrolysis furnace and the ammonia injection grid, which seriously affects the long-term safe and stable operation of the denitrification device. Therefore, an in-depth understanding and accurate judgment of the cause of the crystallization blockage of the urea pyrolysis system has important theoretical and practical significance for the optimization and adjustment of the denitration system.

2. Urea pyrolysis process introductions
Urea (NH₂CONH₂) is a white or light-yellow crystal, which can be decomposed into NH₃ and CO₂. Ideally, urea directly thermally decomposed into NH₃ and isocyanic acid (HNCO), and HNCO hydrolyzed into NH₃ and CO₂, as shown in formulas (1) and (2)[1]:

\[
\text{NH}_2\text{CONH}_2 \rightarrow \text{NH}_3 + \text{HNCO} \quad (1)
\]

\[
\text{HNCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2 \quad (2)
\]
According to related literature studies, urea begins to decompose at 152 °C [2]. Biuret begins to form at 150 °C to 190 °C. When the temperature rises to 190 °C to 250 °C, the biuret starts to decompose to form cyanuric acid, cyanuric acid monoamide and cyanuric acid diamide. When the temperature exceeds 250 °C, cyanuric acid begins to decompose and gradually transform into cyanuric acid monoamide, cyanuric acid diamide and melamine [3-5]. When the temperature rises to 300°C-700 °C, cyanuric acid and its homologues gradually decompose completely [6].

3. Brief introduction of the unit

A power plant in Hunan is a 2×660MW ultra-supercritical boiler, and the denitration project adopts SCR technology. The SCR denitration system adopts the method of urea pyrolysis to prepare reducing agent ammonia. Since the two 660MW units put into operation, blockage phenomenon of pyrolysis furnace and ammonia injection pipeline crystallization occurred frequently. In order to explore the blockage reasons, the clogging materials were collected from the pyrolysis furnace and the ammonia injection main pipe, which were named as sample A and sample B respectively. The composition of the two samples were analyzed, characterized and identified to judge the crystal clogging formation cause and conditions.

4. The causes of blockage in pyrolysis furnace and ammonia injection pipeline analysis

4.1. Experimental results analysis

In order to explore the elemental composition and microstructure of the sediment samples, ICP, EDS and XRD, were used.

(1) ICP and EDS results analysis

The two samples were dissolved in deionized water or hydrochloric acid solution, and the content of inorganic elements was analyzed by ICP. The results are shown in Table 1. It can be seen that the higher element content of sample B is Si, Al, S, Ca, Fe, K, and the content accounts for 10%, the other elements are C, N, O, the higher element content of sample A is Si, Al, Ca, Fe, etc., with a mass proportion of 2.3%, the other elements are also C, N, O.

Table 1. ICP-MS all-element analysis results of sediments

| Element mass fraction (%) | Al  | Ba  | Ca  | Fe  | K   | Mg  | Na  | P   | S   | Si  | Sr  | Ti  |
|---------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Sample A                  | 0.99| 0.1 | 0.09| 0.02| 0.03| 0.02| 1.04| 0.02|     |     |     |     |
| Sample B                  | 3.55| 0.01| 0.42| 0.36| 0.1 | 0.05| 0.06| 0.02| 64  | 4.51| 0.03| 0.06|

Table 2. EDS analysis results of sediments

| Element mass fraction (%) | C   | N   | O   | Mg  | Al  | Si  | S   | Ca  |
|---------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Sample A                  | 29.80| 33.79| 35.70| 0   | 0.42| 0.32| 0   | 0   |
| Sample B                  | 25.33| 26.57| 31.77| 0.18| 6.83| 7.51| 0.94| 0.88|

(2) XRD results analysis

Figure 1 shows the XRD analysis results of the samples A and sample B. It can be seen that the two samples are mainly organic crystal structures, and both contain cyanuric acid or its isomers. The
molecular composition is C$_3$H$_3$N$_3$O$_3$. Combining the EDS and ICP test results, it can be determined that C$_3$H$_3$N$_3$O$_3$ is the main component of the sediment samples.

![Figure 1. XRD pattern of sediment](image)

(3) Analysis of sample intermediate product content

Based on a 100g sample, assuming that the molecular composition of the sample is C$_3$H$_3$N$_3$O$_3$, MgO, Al$_2$O$_3$, SiO$_2$, S, CaCO$_3$, and C$_3$H$_3$N$_3$O$_3$ is calculated using nitrogen and oxygen as the calculation standard, the content of each component in both samples is calculated, as shown in Table 3.

| Element              | Sample B $^a$ | Sample A $^a$ | Sample B $^b$ | Sample A $^b$ |
|----------------------|--------------|--------------|--------------|--------------|
| C$_3$H$_3$N$_3$O$_3$ (%) | 41           | 94           | 7            | 94           |
| Other oxides (%)     | 51           | 6            | 80           | 6            |
| Elemental sulfur and salts (%) | 8           | --           | 13           | --           |

$a$: C$_3$H$_3$N$_3$O$_3$ is calculated based on nitrogen; $b$: C$_3$H$_3$N$_3$O$_3$ is calculated based on oxygen

It can be seen from Table 3 that regardless of C$_3$H$_3$N$_3$O$_3$ based on nitrogen or oxygen, the two calculation results of the sample A and sample B are not much different. Among them, cyanuric acid accounts for up to 94%, indicating that the impurities of pyrolysis furnace were brought from urea pyrolysis intermediate product, water insoluble matters and other impurities. After long-term accumulation, the proportion of pyrolysis intermediate increased. So element N and element O mostly come from the pyrolysis intermediate product, only a small part of element O come from metal oxides. Sample B content 7%-41% cyanuric acid and 51% or even higher other components. This is because the problem of ash leakage at the ammonia injection main pipe is more serious than in the pyrolysis furnace. At the same time, the amount of intermediate product deposited in ammonia injection main pipe is little, the sample composition is complicated, and element nitrogen may exist in other forms. Therefore, the calculation results based on oxygen and nitrogen have a significant gap.

4.2. Cause analysis of crystal blockage

(1) Source analysis of C$_3$H$_3$N$_3$O$_3$

In the process of urea pyrolysis, temperature is the main factor that affect the formation of crystal and their composition distribution. HNCO is the pyrolysis product of urea, it can exist stably in the gas phase. Only when the reaction temperature is higher than 400°C or under a specific metal or metal oxide catalyzed, HNCO can further reacted to produce NH$_3$[7]. When the temperature lower than 400°C, HNCO will be undergo polymerization, depolymerization or other subsequent reaction to produce intermediate
by-products such as biuret, cyanuric acid, and melamine. These solid white substances are insoluble in water and difficult to remove.

According to relevant literature [8], cyanuric acid and its homologues are produced at a temperature of 190°C to 350°C. If the flow field in the urea pyrolysis furnace is uneven, or the urea solution has poor atomization effect, a large amount of intermediate reaction products will be produced, especially at the tail of the pyrolysis furnace. A large amount of cyanuric acid cannot be decomposed in the pyrolysis furnace at low temperature, and it deposited on the metal wall of the pyrolysis furnace and outlet pipe. In addition, if the heat preservation or heat tracing effect of the equipment is poor, the water vapor and ammonia in the pipeline will condense and accumulate in the pipeline, which will also cause blockage.

The ammonia injection control system of the denitrification device generally adopts fixed ammonia nitrogen molar ratio or a fixed SCR outlet NOx mass concentration control method. Due to the delayed feedback of the catalyst reaction in the SCR reactor and the delayed response of the NOx analyzer, it is difficult to accurately control the amount of ammonia injection. In order to meet the requirements of ultra-low emissions, the pyrolysis volume of urea is often increased, leading to the temperature field and flow field distribution deteriorated, the temperature in some areas may be lower than 300 °C, which makes the urea unable to be completely pyrolyzed and the atomization effect becomes worse.

2) Source analysis of fly ash

The hot primary air from air preheater is used as the heat source of the urea pyrolysis system, however, the primary air may be mixed with fly ash due to the air preheater can not tightly sealed. The ash in the hot primary air not only affects the flow field distribution of the entire pyrolysis chamber, but also easily combines with the small particle size urea solution to form an initial crystalline layer, which prevents the urea from being completely pyrolyzed. Once the deposits formed, the flow field in the pyrolysis furnace will be affected, which will accelerate the formation of urea intermediate products.

The quality of compressed air, dissolved water and urea raw material is also an influencing factor. If the content of mineral dust, oil are higher, these tiny insolubles may deposited on the spray gun nozzle, resulting in poor atomization effect or even clogging spray gun.

5. Conclusions

In view of the clogging of urea crystals phenomena, sediment samples were collected from the pyrolysis furnace and the ammonia injection main pipe, and detailed characterization and analysis were carried out to identify the composition of the sediments and determine the cause of the crystallization clogging. The analysis of the chemical composition of the sample shows that the main component is cyanuric acid, and contains Si, Al, Ca, Fe and other substances. Among them, cyanuric acid is an incomplete product of urea decomposition. Si, Al, Ca, Fe and other substances may originate from primary air leakage, impurities in urea or dissolved water, and the problem of ash leakage at the ammonia injection main pipe is more serious than that in the pyrolysis furnace, the deposition amount of intermediate products at ammonia injection main pipe is smaller and the sample composition is complex.

In order to reduce the occurrence of crystallization blockage, the control system of the pyrolysis furnace should be optimized, and the working status of the urea atomization nozzle should be checked regularly to ensure that the pyrolysis temperature is maintained above 350°C to ensure the sufficient urea solution atomization effect and sufficient pyrolysis reaction.

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