Prevention and Countermeasures of Urea Crystallization in SCR Urea Pyrolysis System

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Abstract. The reasons for urea crystallization in the SCR urea pyrolysis system are analyzed, and system design, flow field control, equipment selection, process water and compressed air quality requirements and other aspects are optimized and selected, in order to improve the urea crystallization of pyrolysis furnace Phenomenon to effectively prevent and provide targeted countermeasures. In the process of pyrolysis of urea to produce ammonia, a slight deviation will easily form crystals. In severe cases, pipeline blockage and insufficient ammonia supply in the system will occur. However, based on the feedback of multiple application projects in the past ten years, there has not been a situation that has affected the operation of the pyrolysis system due to serious urea crystallization, and as long as the system design, flow field control, equipment selection, process water and compression Optimization and selection of air quality requirements and other aspects can effectively prevent and control the phenomenon of urea crystallization. The urea pyrolysis ammonia production system is a safe and effective source of ammonia, which can ensure the long-term safe and stable operation of the SCR system, so it will be more and more widely used.

1. Introduction
The newly revised "Air Pollutant Emission Standard for Thermal Power Plants" implemented on January 1, 2012 stipulates that the NO emission concentration of units put into operation or approved before December 31, 2003 shall not be greater than 200mg/Nm3, and then active or newly built The NO emission concentration of the unit shall not be greater than 100mg/Nm3. With the implementation of strict new standards, the flue gas denitration system has become one of the indispensable equipment in thermal power plants. Selective Catalyst Reduction (SCR) has become a power plant denitration due to its high denitrification efficiency. The technology of the project is the first choice, and it has been more and more widely used [1-2].

There are three sources of reducing agent NH3 in SCR technology: liquid ammonia (anhy- drous Ammonia), ammonia (Aqueous Ammonia) and urea (Urea). Since liquid ammonia is a dangerous chemical, as the country pays more and more attention to safety, a series of related restrictions have been gradually introduced, making the use of liquid ammonia in power plants more and more subject to approval, construction period, and land occupation. Restrictions, the procedures for passing environmental protection acceptance after being put into operation are also more cumbersome; ammonia water is also subject to application limitations due to its high operating costs. As a non-hazardous raw material for ammonia production, urea has the same denitrification performance as liquid ammonia, is...
a green fertilizer, non-toxic, and can be used completely, so there is no legal restriction, and it is easy to transport, store and use. At present, the use of urea as a reducing agent for SCR denitrification in China has become a trend and has gradually become the mainstream, especially in some key areas and urban power plants close to residential areas, which have been increasingly used [3-4].

2. Brief introduction of urea hydrolysis and pyrolysis technology
There are usually two methods for preparing ammonia from urea: pyrolysis and hydrolysis. The hydrolysis method decomposes urea in the form of an aqueous solution. The pyrolysis method is to decompose the urea solution after direct heating and atomization.

2.1. Urea hydrolysis technology
Urea hydrolysis mainly adopts the AOD method and U2A method. The AOD method started in 1996-1997. The U2A method started approximately in 1999. The first demonstration projects of both methods were built in 2000. The disadvantage of urea hydrolysis technology is that it requires high-pressure equipment and complex wastewater treatment system, and will produce biurea, 1,3-dicarbamoylurea, cyanuric acid (Biurea, Triuret, Cyanuric Acid) and other polymers along with the reaction. These by-products will stick together with the "popcorn-like" fly ash, which can easily cause blockage of the catalyst. As the problems of high pressure, blockage, corrosion and system complexity have not been completely solved for a long time, the urea hydrolysis process with high defect rate is becoming more and more difficult to be accepted by customers, so it is gradually withdrawing from the market. Compared with this, the urea pyrolysis process has developed rapidly, and its engineering application has been continuously expanded [5-7].

2.2. Urea pyrolysis technology
At present, more and more power plant catalysts tend to adopt urea pyrolysis technology, and urea pyrolysis currently mainly adopts NOxOUT ULTRA method. NOxOUT ULTRA is the registered name of a U.S. fuel company (Fuel Tech Inc.) for the pyrolysis of urea to produce ammonia. At present, the urea pyrolysis system has a performance of more than 40 units in China, and the largest unit capacity is the $4 \times 1000$MW unit of Huaneng Yuhuan Power Plant that operated in 2010.

Beginning in 2006, Huaneng Beijing Thermal Power Co., Ltd. implemented flue gas denitrification technology for its 4 830t/h coal-fired boilers, and designed the SCR system of 4 units to share a set of reducing agent storage, preparation and supply equipment, using NOxOUT ULTRA urea heat De-ammonia technology, this is the first domestic project that uses urea pyrolysis to decompose reducing agent for SCR flue gas denitration.

The main equipment of the urea pyrolysis system includes urea storage bin, urea dissolution tank, urea solution storage tank, dilution fan, urea solution nozzle, pyrolysis furnace and electric heater (fuel or gas heater can also be used), the main process flow The solid urea is dissolved and configured into a 40%-60% urea solution. The mixing/feeding pump transports the urea solution to the urea solution storage tank. The urea solution is sprayed into the pyrolysis furnace by a specially designed spray gun and decomposed into NH3, the heat required for pyrolysis comes from the hot primary air or secondary air heated by the heater. The dilution air delivered by the dilution fan is mixed with the ammonia obtained by decomposition to form an ammonia/air mixture with an ammonia concentration of less than 5%. Ammonia Injection Grid (AIG) is injected into the flue gas system.

3. Analysis of the causes of urea crystallization in pyrolysis furnace
According to the tracking feedback of dozens of sets of urea pyrolysis systems at home and abroad, it is learned that the urea pyrolysis system is safe and stable in operation, and there is basically no need for offline maintenance during operation. However, some pyrolysis systems found honeycomb deposits at the bottom and tail pipes of the pyrolysis furnace during the shutdown of the unit for maintenance. According to the laboratory test, the deposits were urea crystals. The performance during operation was the pressure difference between the inlet and outlet of the pyrolysis furnace. Slightly increase. The two
important factors of pyrolysis are sufficient heat and better atomization effect of urea solution. The mechanism of urea formation without pyrolysis is more complicated. According to the analysis, there are mainly the following reasons:

3.1. Design problems of flow field inside the pyrolysis chamber
Deviation in the design of the pyrolysis chamber, on the one hand, may lead to uneven internal flow field distribution, incorrect temperature field control, and local low temperature in the pyrolysis chamber to form urea crystals; on the other hand, it may lead to the residence time of the atomized urea solution in the pyrolysis chamber If it is too short, part of the unpyrolyzed urea will crystallize at the end of the pyrolysis chamber.

3.2. Poor atomization effect of urea spray gun
The urea spray gun is one of the key components of the urea pyrolysis system. Whether the spray gun atomizes the urea solution directly affects the conversion rate of urea to ammonia. The atomization effect of the urea spray gun is not good, which can easily lead to the occurrence of urea crystallization.

3.3. Poor quality of urea dissolved water
If the content of minerals and ions in the dissolved water of urea is relatively high, on the one hand, it will promote the crystallization of urea, on the other hand, impurities and ions will also affect or poison the active components of the SCR catalyst.

3.4. The air quality of urea solution atomization is poor
If the quality of compressed air used for urea atomization is poor and the contents of oil, water and dust in the atomized air are high, the float flowmeter will be easily blocked after a long running time. The float flowmeter will not alarm and the urea solution will not be atomized. Entering the urea pyrolysis furnace will affect its pyrolysis effect, and urea crystals will be deposited on the tail pipe of the pyrolysis furnace.

4. Prevention and countermeasures of urea crystallization in pyrolysis furnace
According to the reasons for the formation of urea crystallization in the tail of the pyrolysis furnace, through theoretical analysis, experimental research and engineering examples, the following countermeasures for effective prevention of urea crystallization in the pyrolysis furnace are proposed.

4.1. Reasonably designed flow field of pyrolysis chamber
In order to ensure that the urea solution can be completely gasified, mixed and decomposed in the pyrolysis chamber, computational fluid dynamics (CFD) with a droplet trajectory model should be used in the design of the pyrolysis furnace, combined with a chemical kinetic model (CKM) for modeling, to achieve reasonable and optimized design links to the greatest extent, to ensure the operation effect after project implementation, and effectively avoid defects such as urea crystals caused by process design.

4.2. Ensure the atomization effect of urea spray gun
Through experimental research and comparison and user feedback on engineering projects, the imported urea spray gun with patented technology is indeed superior in terms of atomization effect of urea solution, nozzle blockage prevention, and service life. Ensuring the atomization effect of the urea solution is the key to ensuring the conversion rate of urea to ammonia and preventing urea crystallization.

4.3. Improve the quality of urea dissolved water
The water quality requirement of urea dissolved water is water hardness \( \leq 150 \text{ppm} \) (expressed as CaCO3), generally deionized water or demineralized water is used. If the mineral and ion content in the water does not meet the requirements, you can consider adding some additives to improve the dissolution
The quality of water. Ensuring the quality of urea dissolved water can effectively enhance spray atomization, minimize the precipitation of urea due to impure water, and prevent urea from crystallizing.

4.4. Ensure the air quality of the atomized urea solution
There are two types of compressed air commonly used in thermal power plants: instrument air and miscellaneous compressed air. Miscellaneous gas has a wide range of uses and low quality. Generally, the pressure is 0.7MPa, the maximum particle size is 40 μm, and the maximum particle concentration at room temperature is 10mg/m³. The water vapor content in the air is expressed by the pressure dew point, and the maximum pressure dew point is 10°C. The oil content is 25mg/m³. The instrument air is compressed air for control instruments and pneumatic instruments. The quality is good. The pressure is 0.7MPa, the maximum particle size is 1μm, the maximum particle concentration at room temperature is 1mg/m³, the maximum pressure dew point is -40°C, and the maximum oil content is 1mg/m³. There is still a certain gap between the quality of miscellaneous air and instrument air. It is recommended to use instrument air for urea solution atomization air, which can effectively prevent urea crystallization due to high oil, water and dust in the air.

5. Engineering examples
A power plant has 4 200MW extraction steam heating units, each equipped with a 670t/h coal-fired boiler. From 2007 to 2008, in accordance with environmental protection requirements, the four furnaces of the power plant were successively undergone denitration transformation. After detailed economic and technical comparison, the urea pyrolysis SCR process was finally selected.

The urea pyrolysis system is designed according to the ammonia demand of each furnace 160kg/h, and there is a 10% margin. The 100% urea consumption is 296kg/h. The size of the pyrolysis furnace is: \( \Phi 2.3m \times 12.5m \). Combustion light diesel heater is used as heat source, fuel consumption is 107kg/h, dilution water consumption is 296kg/h, and atomized compressed air consumption is 120Nm³/h. The denitrification system of the first furnace was put into operation in May 2007 and passed the acceptance inspection, reaching a denitrification efficiency of 83%. The urea pyrolysis system is safe and stable. During a minor repair of the unit in 2008, the inspection found that there were deposits in the lower part of the urea pyrolysis furnace near the furnace wall. The deposits were relatively hard, had pores, and formed a honeycomb shape. Upon inspection, the urea crystals were found. After the technicians understood the on-site operation, they found that the urea pyrolysis system used dissolved water as cooling water, which was of poor quality; and the compressed air was miscellaneous air. After the maintenance, the air supply source of the atomizing air was replaced, the original miscellaneous air was replaced with the instrument air, and the operation status of the compressed air system was checked regularly, and timely maintenance was performed to ensure the cleanness and smoothness of the system. The actual use situation shows that this method can effectively solve the problem of clogging of the tail pipe of the pyrolysis furnace.

6. Conclusion
In the process of pyrolysis of urea to produce ammonia, a slight deviation will easily form crystals. In severe cases, pipeline blockage and insufficient ammonia supply in the system will occur. However, based on the feedback of multiple application projects in the past ten years, there has not been a situation that has affected the operation of the pyrolysis system due to serious urea crystallization, and as long as the system design, flow field control, equipment selection, process water and compression Optimization and selection of air quality requirements and other aspects can effectively prevent and control the phenomenon of urea crystallization. The urea pyrolysis ammonia production system is a safe and effective source of ammonia, which can ensure the long-term safe and stable operation of the SCR system, so it will be more and more widely used.
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