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Research/Technical Note

Reason Analysis and Countermeasures of Coal-Fired Power Plant Denitrification Ammonia Injection Valve Blockage

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Abstract: This paper introduces the technological process and operation mode of denitrification and ammonia supply in coal-fired power plants. The Selective Catalytic Reduction (SCR) flue gas denitrification technology of coal-fired power plant is a great significant to environmental protection, which denitrification efficiency is up to 90%. A coal-fired power plant SCR boiler flue gas denitrification device of ammonia controlling valves often block in the winter, and need stopping the device to carry out manual cleaning, that seriously affecting the normal operation of the SCR system and NOx emissions standards. Through the mothed of analyzing of the physical scale components of liquid ammonia quality, environmental temperature, equipment, material, jam, we had found the causes of the problem. Ammonia injection valves plug is mainly made of carbon steel rusting and ammonia supplying of inner tube in oily volatile mixed cause. According to the actual situation of the equipment in the power plant, the operation mode of liquid ammonia evaporator was adjusted, the denitrification ammonia suppling pipeline was purged, the structure of ammonia injection regulating valve was reformed, and the stainless steel-pipeline was replaced. The retrofitting reason of ammonia injection regulating valves and their structure are introduced in detail, which is the key to solve the problem.

Keywords: Ammonia Injection Valve Structure, Ammonia Evaporator, Blocking, Scale Sample Analysis, Improvement

1. Introduction

A coal-fired power plant has seven power units with an installed capacity of 5×330MW+2×1000MW, which is No. 8~14. The 330 MW power units were designed and made in Shanghai Electrical which were forced circulation type Π subcritical drum boiler; The 1000MW units were a supercritical tower type boiler which were also designed and manufactured by Shanghai Electric which were put into operation in June 2011 and May 2012, and designed with 100% flue gas SCR denitrification system. The SCR is considered as a mainstream technology of flue gas denitrification in thermal plant which was widely used in Europe and Japan, and the denitrification efficiency is up to 80%~ 90%. [1] From 2012 to 2014, all 330MW units were gradually transformed and added 100%SCR flue gas denitrification system. All the 7 units of denitrification catalyst were set according to 2+1, with high dust setting, reducing agent as liquid ammonia and catalyst as honeycomb. Each unit is equipped with a complete set of ammonia injection system, including eddy current mixer and ammonia control valve. [2] During the winter or spring and autumn period, the ammonia control valve of the power plant is often blocked, which affects the normal operation of the SCR flue gas denitrification system. The causes of the problem are analyzed below and solutions are proposed. Since the plant took corresponding preventive measures in June 2014, there has been no further blockage of the regulating valve.

2. Introduction to Ammonia Supply System

The ammonia station of a coal fired power plant was designed by a chemical design institute in 2009 in accordance with the capacity of 7 units for ammonia production. It was built in line with the 2 x 1000MW unit and put into operation in June 2011. The ammonia station is mainly composed of liquid ammonia storage system, liquid ammonia evaporation system and waste water discharge system, [3] liquid ammonia storage capacity is 3 x 150m3, and liquid ammonia evaporation capacity is 3 x 850kg/h. The liquid ammonia evaporator adopts the surface type heating method of disc tube. Heating steam source parameters: 0.6 ~ 1.3MPa, 150 ~ 170°C, liquid ammonia using discontinuous supplementary way to join the evaporator. Ammonia station and ammonia system are the products of early design and manufacture in China. All valves, pipes and pressure vessels are made of carbon steel.

2.1. Ammonia Plant Operation Process Flow

Liquid ammonia is transported by tank car and pressurized by compressor to storage tank. The liquid ammonia is exported from the bottom of the tank to the evaporator, which is heated and evaporated into gas ammonia. The gas ammonia enters the bottom of the gas ammonia buffer tank from the top of evaporator, and then is sent to the SCR flue gas denitrification system of each unit through the ammonia supply pipeline at the outlet of the top of the gas ammonia buffer tank. [4] The process flow of SCR flue gas denitrification is shown in Figure. 1

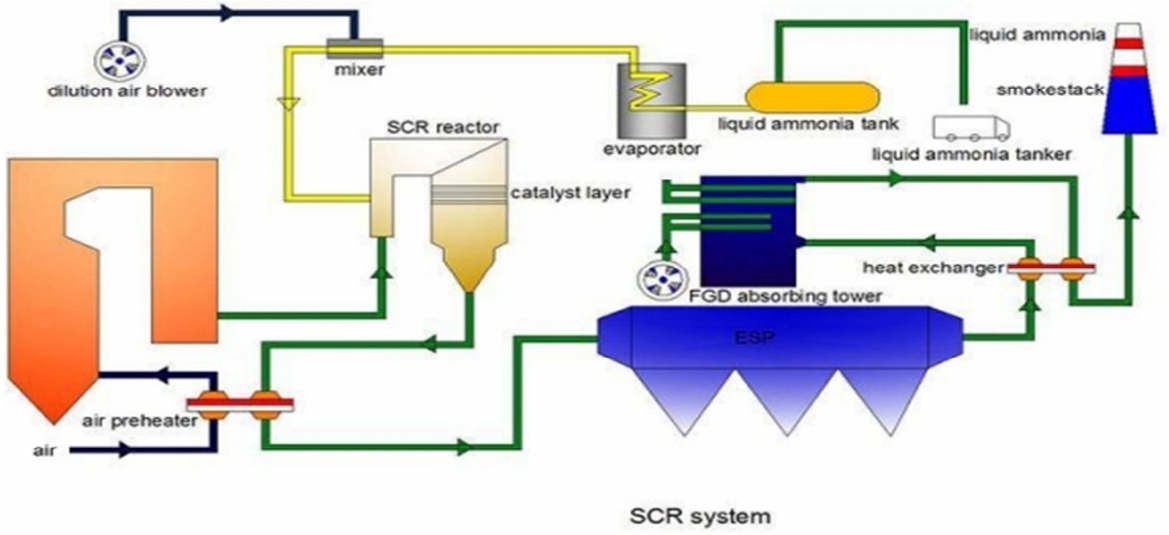

Figure 1. *Flow chart of denitrification SCR technology.*

2.2. Main Operating Parameters of Ammonia Station

The pressure of the liquid ammonia evaporator is automatically adjusted through the steam regulating valve, and the pressure setting value is 0.55MPa. Ammonia gas outlet temperature generally in 40 ~ 50°C, temperature fluctuation is mainly because the evaporator puffing in liquid ammonia, ammonia temperature can drop a short period of time, or load change ammonia injection quantity adjustment. Because of the large number of units in the plant, the changes in the amount of ammonia injected by a single machine have little influence on the evaporation system, and the pressure and temperature are relatively stable in the operation.

3. The Side Spray Ammonia Valve Is Blocked

3.1. The Situation

In November 2012, the factory 14 units (1000 mw) happens first spraying ammonia valve jam, denitrification system can run normally for a period of time after cleaning up, with the increase of operation time, jam frequency increased. After that, the SCR ammonia injection regulating valve of other units also began to be frequently blocked, and the disturbance treatment was invalid by closing the valve back and forth and opening the full ammonia injection regulating valve, sometimes two or three times should be cleaned in one day. Spraying ammonia valve block position in the valve core, the shrouded (similar to the restrictor), a blockage to dark brown or khaki, block and powder, have certain adhesion, block can crush, clogs in addition to some unit with gray block, there is a little black particles (see figure 2, 3).

Figure 2. *Brown black blockage in the ammonia injection control valve.*

Figure 3. *Khaki blockage dissolved in water.*

3.2. Analysis of Blockage Composition

Finding out the cause of blockage is the key to solve the problem. First of all, the sampling analysis of all the injected ammonia control valves. The plugging material can be adsorbed by magnet. The ammonia smell is very heavy and oily, indicating that there is iron or iron oxide in the plugging material. A small amount of plugging material was taken for water solubility analysis. About half of them are volatile matter. The other half are granular residues that are completely soluble in hydrochloric acid and are basically iron oxides. It can be inferred that oxides are the corrosion products of ammonia equipment. The fouling samples were sent to Jiangsu provincial power research institute for further scale analysis, and the burn reduction was 50.5%, and the residue composition was shown in table 1.

Table 1. *Scale sample analyzing composition table of SCR ammonia injection control valve.*

Mass fraction	Numerical (%)
Fe_2O_3	96.60
CuO	0.01
Al_2O_3	0.31
MnO	0.43
SiO_2	1.36
CaO	0.39
P_2O_5	0.1
SO_3	0.65
Cr_2O_3	0.06
TiO_2	0.02
NiO	0.02
K_2O	0.04

4. Analysis on the Cause of Blockage of Ammonia Valve

4.1. Effect of Liquid Ammonia Quality

According to the <Guide for the flue gas denitrification technology in thermal power plant> (DL/T 296-2011), [5] the quality of denitrification reducer must meet the technical standard of <Liquefied anhydrous ammonia> (GB536-1988). [6]

Therefore, tank car unloading ammonia before sample analysis, the first sight is colorless transparent liquid, on the bottom, according to the <Determination of liquefied anhydrous ammonia-Part 4: Residue content titrimetric method > (GB/T 8570.4-2010), [7] analysis result purity was greater than 99.6%, residue content < 0.4%, meet the requirements. The internal inspection of No. 2 liquid ammonia storage tank, No. 1 evaporator and No. 1 gas-ammonia buffer tank is carried out for the first time in March 2014. There is no sediment at the bottom of the liquid ammonia tank, and there is a thin layer of oily sediment at the bottom of the air ammonia buffer tank. The bottom of the evaporator is 5 ~ 8cm thick sediment. Analysis on burning reduction of bottom sediment of evaporator: 77% of volatile matter; The residue is soluble in hydrochloric acid, i.e., 22.1% of the sediment is iron oxide; The oil deposits at the bottom of the buffer tank are viscous and are basically combustible volatiles. It can be judged that combustible volatiles come from liquid ammonia, which can be divided into organic compounds, such as oil, hydrocarbon, etc., but none of these substances will react with iron. According to the redox theory, both iron and ammonia are reductive substances, and the redox reaction and electrochemical reaction will not occur without water and oxygen. [8] Liquid ammonia sample is clear and transparent, indicating that there are few granular impurities, so the iron rust in the sediment mainly comes from the original corrosion products of the evaporator drum wall, and the total amount is limited. Therefore, it is believed that the blockage of ammonia injection regulating valve is mainly caused by the oily substances in liquid ammonia.

4.2. Effect of Evaporator on Impurities

Evaporator evaporation gas ammonia from the top into the buffer tank bottom evaporator, again by the top into the buffer for ammonia pipeline, and then after a long pipeline to SCR flue gas denitrification system, if the gas in the ammonia containing particulate impurities, such as rust, so rust at the bottom of the evaporator impurity content is high, the bottom of the buffer tank should have a lot of impurities, rather than a thin layer. So those impurities carried by gas ammonia in the liquid ammonia evaporator blocked spraying ammonia valve possibility is very small, the injection of ammonia the regulator of the solid particles clog comes not from liquid ammonia and ammonia station equipment itself, and oily volatile substances can bring into the gas ammonia for ammonia pipeline.

4.3. Effects of Residual Ammonia Pipeline Installation

The plant SCR flue gas denitrification system for seven units of spray ammonia are supplied by two same evaporators, but not all of the spray unit ammonia valve have congestion, No. 8~10 units ammonia by single pipe supply, No. 11~12 and No. 13~14 units public a mother tube, respectively. When the ammonia supply pipeline of No. 13 unit is laid out, it will be put into use immediately. No. 14 unit will be put into operation at the end of the ammonia supply master pipe and the pipeline will be empty for one year. The ammonia supply pipeline of unit 10 is laid at the same time, and the pipeline of No. 9 unit is put into operation half a year after it is empty. The

clogging frequency of unit 9 is higher than that of No. 10 unit. So, laying good less carbon steel pipe wall corrosion, which was put into operation, blocking is not serious, and empty time long carbon steel pipeline corrosion is serious, power station denitrification bullishness of ammonia wash after a period of time, the lining of corrosion products falling off, bullishness of ammonia flow carries the block valve. At the same time, the inspection of ammonia pipe cutting showed that the pipe at the outlet section of buffer tank was relatively smooth, with little iron rust and a thin oil attachment on the surface. There is a layer of gray attachment on the inner wall of the ammonia supply horizontal pipeline about 200m from the SCR regulating valve and it has been peeled off. It will break and fall off when touched lightly.

4.4. The Effect of Ambient Temperature

SCR spraying ammonia valve jams happen most at the time of low temperature, while the ammonia evaporator outlet gas temperature is the lowest in more than 40°C, but SCR area ammonia pipeline layout in an open area outside the furnace, and platform in the wind is bigger, the environment temperature is low, the pipe wall attachments to cold strip rust and oily, bullishness of ammonia flow to use SCR regulating valve, at the same time due to the tube temperature is reduced, the gas ammonia density increases, the velocity is relatively lower, don't have enough kinetic energy to inject the gas ammonia stripping into SCR system; Due to the blockage of the regulating valve core, this solid material was deposited at the throttle hole of the valve core. In addition, ammonia gas was oily and sticky, mixed with sediment, and finally blocked the regulating valve.

4.5. Influence of SCR Ammonia Injection Valve Structure

The factory used spraying ammonia regulator is shrouded type throttle valve, up and down through the control valve core position, control over all round orifice size to realize automatic spraying ammonia flow rate adjustment, regulating valve jams cleaning before and after pictures as shown in figure 4, 5. As can be seen from figure 4, the blockage mainly occurs at the throttle hole of the regulating valve. Ammonia valve throttling cover in the factory there are three kinds of structure (see figure 6~8), No. 13 and No. 14 units using the structure before retrofit, No. 9 and No. 10 units using the first transition structure, No. 11 and No. 12 units using the 2nd modification of structure. No. 9 and No. 10 units put into operation after spraying ammonia valve occasionally congestion, No. 8,11 and No. 12 units of commissioning spraying ammonia valve has not occurred since the congestion, enveloped to remove the original frames, the original four directions of three small throttle a large orifice. The denitrification transformation time of unit No. 8 is the latest, and the regulating valve is the same as unit No. 11 and No. 12. Before unit No. 8 was put into operation, because the ammonia supply pipeline was empty for a long time, high temperature steam and compressed air were used to clean the pipeline.

Figure 4. *Ammonia injection control valve cover before cleaning.*

Figure 5. *Ammonia injection control valve cover after cleaning.*

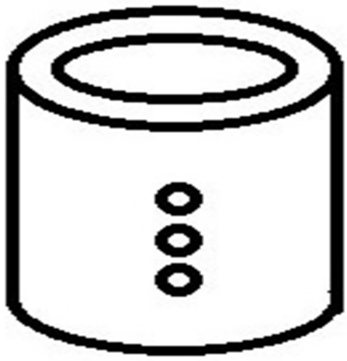

Figure 6. *The structure of Ammonia injection control valve cover before the reforming.*

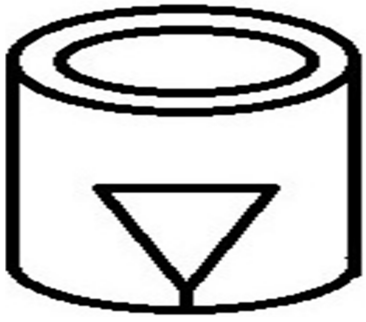

Figure 7. *The structure of Ammonia injection control valve cover after the first reforming.*

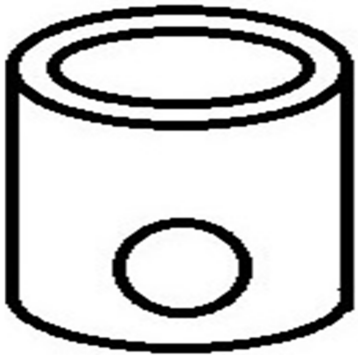

Figure 8. *The structure of Ammonia injection control valve cover after the second reforming.*

4.6. Cause of Blocked Ammonia Valve

The main reason for the blockage of ammonia injection regulating valve in this factory is that the ammonia supply pipe is made of carbon steel, and the original iron rust on the inner wall is washed off by gas ammonia. Plus there is a small amount of oily material in the liquid ammonia, with liquid ammonia evaporation, in the process of flow with the decreasing temperature and condensation adhesion on the pipeline internal strip rust and sediment, the sediment increased flow to drive like a snowball rolling bullishness of ammonia, when big enough or rally after a certain amount, eventually plug in spraying ammonia valve throttle hole; Under the condition of the orifice are partially blocked, regulating valve will automatically open, but due to the structure of the regulating valve, ammonia injection process can't wash it clogs, causing blockage is piling up, eventually all the valve closed, need artificial collapse of cleaning. Under the condition of no moisture and oxygen, ammonia and iron does not react redox reaction, so it can be concluded that, the carbon steel for ammonia pipeline if not empty, i.e. not in contact with air, ammonia injection valve block, after a certain number of jam frequency will be less and less, until the inside tube wall rust and sediment by gas ammonia will be blocked after washed clean, this period may be a long time. That's why the new installation of carbon steel pipeline jam frequency less or not, and vacancy for a period of time of carbon steel pipe valve plug had occurred in the season of the temperature change is big, the heat-expansion and cold-contraction rust and easy to make the inner wall of pipeline caused by sediment detachment.

5. Response

(1) Strictly control the quality of liquid ammonia and use Lysenko liquid ammonia purity analysis method to analyze liquid ammonia purity periodically to ensure that liquid ammonia quality is qualified. [9]

(2) Liquid ammonia evaporator and air ammonia buffer tank shall be discharged regularly once a week to minimize the amount of sediment deposited at the bottom of evaporation tank and buffer tank carried by liquid ammonia evaporation. Meanwhile, liquid ammonia storage tank, evaporation tank and buffer tank are isolated and cleaned regularly once a year.

(3) The advantage of overhaul will be part of the unit for ammonia pipeline replacement for stainless steel pipe, the practice also proved that using stainless steel for ammonia pipeline spraying ammonia valve without clogging, such as Taizhou Power Plant. For the unit undergoing denitrification transformation, the ammonia pipeline should be used to flush the pipe with high temperature steam before it is put into operation, and then the compressed air should be used to dry the residual water in the pipeline.

(4) The winter air temperature is lower, three run in parallel with the evaporator, and reduce the evaporation rate of a single evaporator, at the same time by increasing the ammonia gas pressure in the evaporator, achieve the goal of improve the outlet temperature of the gas ammonia. It can prevent the sediment in the oil substance condensation adsorption pipeline from being too low temperature, high density and low flow rate of gas ammonia in winter. Ammonia gas outlet temperature shall generally be from 35 ~ 50°C to 60-75°C. Strengthen daily inspection and repair the thermal insulation facilities timely.

(5) For the units that have been blocked by the ammonia injection regulating valve, replace the regulating valve and adjust the flow rate from the original throttle cover to the valve stem valve core opening. When the ammonia injection regulating valve is cleaned, the door core and shroud must be cleaned, otherwise the remaining plug will adhere to the oily substances in the gas ammonia, causing the valve to be fouled again quickly. At the same time, ammonia gas can be used to purge the pipeline, control the time, prevent the escape rate of ammonia from being too high, prevent the corrosion of ammonium hydrogen sulfate and block the air preheater. [10]

(6) During the temporary maintenance of the unit and the mediation of the unit, clean up the ammonia injection regulating valve, flow meter, filter screen of diluting fan and other equipment to prevent impurities from piling up and blocking the equipment.

6. Conclusion

In this paper, the research results show that the coal-fired units SCR denitrification system for ammonia pipeline using carbon steel material, and not be put into use in a timely manner after pipe installation, plus there is a small amount of oily substance in liquid ammonia, spray is the main reason for the ammonia valve block. After a power plant adopted the above series of countermeasures, the problem was solved, and no ammonia supply regulating valve blockage occurred from November 2014 to May 2016. The experience of this paper is effective and can be used for reference.

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