Study on Comparison and Selection of SCR Denitration Reductant's Preparation System in Heat-engine Plant

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Abstract. SCR denitration reductant's preparation system is the supporting system in heat-engine plant producing reducing agent. Its safety, reliability and stability are crucial. Based on the aspects of technology and economy, this paper makes a detailed comparison and selection of three kinds of denitration reductant's preparation system. They are liquid ammonia process for caustic soda purification, urea pyrolysis and urea hydrolyzation, and finally draws the conclusions.

1. Introduction

The control of NOx will be a key point of environmental protection management after dust and SO_2 in coal-fired power plant. Chinese Environmental Protection Department has completed the research on the NOx emission of thermal power plant in China in 2007, and compiled the "Study on the control technology of nitrogen oxide emission in China Power Plant", as well as propose higher requirements for nitrogen oxide emission limits [1].Now, the mature flue gas denitration technology which is applied to large coal-fired power plant boilers mainly is Selective Catalytic Reduction, and its abbreviation is SCR.SCR denitration reductant's preparation system is the supporting system in heat-engine plant producing reducing agent. Its safety, reliability and stability are crucial.

2.The Introduction of Reducing Agent Preparation System's technology

There are three kinds of denitration reductant's preparation system. They are liquid ammonia process for caustic soda purification, urea pyrolysis and urea hydrolyzation.

The ammonia's construction, operation costs, transportation, unloading, storage, use and other aspects both have security risks. As a result, since 1990s, ammonia has rarely been used as denitration reducing agent. Nowadays, the reducing agent is mainly produced with liquid ammonia and carbamide. And the urea prepare ammonia technology is divided into two kinds of process, pyrolysis and hydrolysis.

2.1 The feature of liquid ammonia and carbamide

Liquid ammonia (NH_3) is widely used in chemical industry, refrigeration and other industries, and there are plenty of mature experiences in using it safely. But because the electric power plants are important and special, we must take fire and safety control measures stricter than other industries when having denitrification project. The placement of ammonia area not only should meet the requirement of Fire Prevention Code for Petrochemical Enterprise Design and Code for Protection Design of Buildings, but also need to set fire sprinkler system, sprinkling system for cooling temperatures in summer and the system for emergency ammonia leakage.

Carbamide ($CO(NH_2)_2$) is generally packed with plastic woven bags, and inside is polyethylene membrane, which achieve moistureproof function, Normal trucks can be used in short distance transport.

2.2 Introduction of Liquid ammonia technique

Liquid ammonia is transported to ammonia area by tank-truck for liquid ammonia, and is put

into storage tank by using liquid ammonia uploading compressor. The liquid ammonia in storage tank is evaporated to ammonia by using ammonia evaporator, and again is transported to denitration System. Finally, it becomes a denitration reducing agent.

2.3 Introduction of urea hydrolysis technique

The hydrolysis technique has been used as preparation of denitration reducing agent in flue gas DeNOx project in heat-engine plant all over the world since 1999.There are three kinds of urea hydrolysis techniques, Ammogen from Italy, U2A from the United States of America[2][3], common hydrolysis method and catalytic hydrolysis from China.

Urea hydrolysis reaction is the reverse reaction of the urea production process, and the reaction can be considered as two steps:

(1) $NH_2CONH_2+H_2O=NH_2COONH_4$-15.5KJ/MOL

(2) $NH_2COONH_4=2NH_3+CO_2$+177KJ/MOL

If there is excess water in the urea solution, the excess water speeds up the rate of reaction. In the case of the participation of excess water, the reaction formula of urea hydrolysis shows below.

NH2CONH2+xH2O=2NH3↑+CO2↑+ (x-1)H2O+161.5kJ/mol.

The technological process of production:

Urea granules will be transported into the urea dissolving tank by urea tank trucks which is dissolved into 40~50% mass concentration of urea solution by demineralized water. Afterwards, urea solution is transported into storage tank for stock by urea dissolving pump. The urea solution situated in storage tank flows into hydrolysis module via feed pump, measurement and distribution device to produce NH_3, H_2O and CO_2.The offspring is delivered from ammonia injection system to SCR denitration system.

2.4 Introduction of urea pyrolysis technique

The application of pyrolysis technology in the world is well-known as hydrogen manufacture from NO_x OUT ULTRA urea pyrolysis designed by USA Fuel Tech Company[4].

The storage system of urea solution in both urea pyrolysis and hydrolysis method is the same.The urea solution (Concentration is 50% (wt)) situated in storage tank flows into pyrolysis furnace via solution feed pump, measurement and distribution device, atomization burner etc.It mixes with the heated primary air from electric heater that will produce NH_3, H_2O and CO_2 after decomposition.All products are injected into denitration reactor by ammonia injection system.The main reaction equations：

$CO(NH_2)_2 \rightarrow NH_3\uparrow+HNCO$

$HNCO+H_2O \rightarrow NH_3\uparrow+CO_2\uparrow$

In the process of preparation, the primary air should be heated up to 600℃ or so,which results in high running cost.

3.Comparison on preparation technology of reducing agent

For purpose here, the compared experimental data of liquid ammonia, urea hydrolysis and urea pyrolysis derives from the new construction project of denitration reducing agent preparation system in a coal-fired power plant at the eastern coastal area of China. There are a total of four 500t coal heating units.

Four units in second phase are transformed in order to achieve ultra-low emissions. On the entrance of denitrification system for second phase, NOx concentration is 400mg/Nm^3.The denitration efficiency is designed to 88%.the total ammonia consumption of four units is 300kg/h under designed operation situation.

3.1 Comparison on system security

3.1.1 Liquid Ammonia Process for Caustic Soda Purification

Liquid ammonia is a kind of compressed gas that is highly volatile, flammable and corrosive. When it mixes with the air, explosive mixture can be created.If the mixture exposes to flame and high temperature circumstances, it will lead to combustion explosion. Acute toxicity of ammonia is four-stage. Once the explosions or leaks happen, the ammonia concentration in the air beyond the

safety value, it can cause poisoning events, even to death. According to the severity of leaks, there are influence and harm on the environment on different degrees.Therefore, there is huge potential safety hazard in the procedures of transportation, unloading, storage and so on. The transportation and management of liquid ammonia must strictly obey the relevant provisions of Transportation of Dangerous Goods Code and Management and Safety of Dangerous Chemical Goods.

3.1.2 Urea method

The appearance of urea (CH_4N_2O) is white crystal or powder，whose physical and chemical properties is stable and it is also a good source of ammonia. There is not harmless to people or environment. Its transportation and management are not restricted by national laws and regulations. Urea is a kind of very safety reductant. Almost no special security measures will be taken. It has obvious advantages on safety that reduce the management difficulty of power plant.

The hydrolyzer of urea hydrolyzation is pressure vessel (design pressure ia 2MPa).From the export of urea hydrolyzer to ammonia & air mixer is also the pressure piping. The equipment and piping of urea pyrolysis is under atmospheric pressure so that the security is higher by contrast to the technology.

3.2 Comparison on system reliability

3.2.1 Liquid Ammonia Process for Caustic Soda Purification

This method is mature enough without proprietary technology. Liquid ammonia process belongs to purely physical process. High purity ammonia with stability flow can be obtained, and the whole process can be automated control logically to achieve precise control of ammonia gas flow, thus the denitration efficiency and ammonia escape rate can be under effective control so that it guarantees the downstream of denitration won't create too much NH_4HSO_4, as to avoid effect on the normal operation of the air preheater.

At present, a unit is equipped with set two sets of SCR reactors in general.But the flue gas flow into the two reactors is often uneven.In this situation, the ammonia flow of each reactor can be controlled respectively to ensure the ammonia escape rate of each outlet of SCR reactor.

3.2.2 Urea hydrolyzation

Urea hydrolyzation is a kind of mature foreign method, the process of which is to decompose urea into NH3.There is mature technology of urea hydrolyzation in domestic relevant units gradually.The urea solution is corrosive so that all equipment or pipes contacted with urea should be made of stainless steel 304 or more senior to prevent urea solution getting into crystallization. It necessary to set up with heat pipes and heating device.Due to urea hydrolysis reactor works under the high operating temperature, and it is susceptible to corrosion. In order to avoid corrosion may cause leakage of the equipment, the material selection of hydrolysis reactor should reach 316L.

Urea hydrolyzation belongs to chemical reaction, which requires a large energy consumption, and the pyrolysis products are the mixed gas of NH_3、CO_2 and H_2O.There is headspace of 3~5min (storage volume) NH_3 in hydrolysis reactor to produce a cushioning effect that can partly overcome the shortcomings of long response time for hydrolysis reactor[5][6].

3.2.3 Urea pyrolysis

The urea solution is corrosive so that all equipment or pipes contacted with urea should be made of stainless steel 304 or more senior to prevent urea solution getting into crystallization. It necessary to set up with heat pipes and heating device. Urea pyrolysis process belongs to chemical reaction, which requires a large energy consumption and the pyrolysis products are mixed gas of NH_3, H_2O,CO_2 and N_2.Due to own characteristics of urea pyrolysis, the control accuracy of NH_3 concentration is relatively lower[7].

3.3 Comparison on energy consumption of the system

The system energy consumption of liquid ammonia process, urea hydrolyzation and conventional urea pyrolysis is shown in table 1.

Table 1 Comparison on system energy consumption of liquid ammonia process, urea hydrolyzation and conventional urea pyrolysis.

SN	item	unit	liquid ammonia process	urea hydrolyzation	conventional urea pyrolysis
1	steam consumption	t/t NH3	0.77	5	0.63
2	power consumption	kWh/t NH3	150	500	4333
3	Energy costs	yuan/t NH3	186	1035	1710

Note：[1] Steam quality :0.8MPa，200℃，steam :170 yuan/T；electrovalency : 0.37 yuan/ degree.[2] Urea hydrolyzation and pyrolysis adopts primary air (about 300℃) as diluted air.This part of the energy consumption is not included in the table above.

On the Table above, THE consumption of liquid ammonia process is better than that of urea method.

3.4 Comparison on technical characteristics

Comparison on technical characteristics of liquid ammonia process and urea method is shown in table 2:

Table 2 Comparison on technical characteristics of liquid ammonia process and urea method

ITEM	**liquid ammonia process**	**Urea Hydrolyzation**				**Urea pyrolysis**
		AOD/Ammogen method	**U2A method**	**ordinary Hydrolyzation**	**catalytic Hydrolyzation**	
Reaction temperature	/	180~250℃	140~150℃	140~160℃	135~160℃	350~600℃
Reaction pressure	/	1.5~3.0MPa	About 0.56MPa	0.4~0.6MPa	0.4~0.9MPa	standard atmosphere
Responsiveness	A few seconds	A few seconds	A few seconds	A few seconds	A few seconds	A few seconds
The pressure vessel	Yes	Yes	Yes	Yes	Yes	Yes
formaldehyde-free blocking problem is or isn\'t	NO	Yes	Yes	Yes	Yes	Yes
difference of key equipment	Liquid ammonia tank, liquid ammonia evaporator, ammonia buffer tank	Hydrolyzer, heat exchanger, steam ejector, mist eliminator, static mixer	Hydrolyzer, heat exchanger, condenser	Hydrolysis device, heat exchanger	Hydrolysis device, heat exchanger	Pyrolysis furnace, steam heater
Decomposition way	liquid ammonia decomposed to NH3 by heating，directly delivering to AIG with pressure	Directly inject steam , and heating the urea solution to decompose , then the vapor carrying the product away, it mixed with hot air in the static mixer and delivering to AIG	Heating the urea solution to decompose indirectly in serpentinepipe,then the hot air carrying the product away, delivering to AIG directly	Heating the urea solution to decompose indirectly in serpentinepipe,then the hot air carrying the product away, delivering to AIG directly	Heating the urea solution to decompose indirectly in serpentinepipe,then the hot air carrying the product away, delivering to AIG directly	indirectly heating atomization urea with heat exchanger，then the hot air carrying the product away, delivering to AIG directly

3.5 Comparison on investment of operation economy

Liquid ammonia process, urea pyrolysis and urea hydrolysis method are more mature technology of denitration reductant preparation. In many countries, there is a great running performance that can meet the needs of reductant of flue gas denitration .Taking four 500t coal heating units of a power plant as an example, The initial investment and operation cost of above three kinds of process are well compared, results as listed in table 3.

Table 3 Comparison on operation cost and the initial investment of 5 x 500 t (ammonia : 4x 75 kg/h) coal heating units

SN	Item	Units	Liquid ammonia process	Urea pyrolysis	Urea Hydrolyzation
1	**Raw material consumption yearly**	T/Y	1500	2735	2735
2	**Ammonia supply yearly**	T/Y	1500	1500	1500
3	**Consumption yearly**				
	Power Consumption [1]	KWH /Y	5×10^5	70×10^5	7×10^5
	steam	T/Y	1160	940	7500
	Demineralized water	T/Y	-	2735	2735
4	**Static investment**	**thousand-yuan**	**~9000**	**~28000**	**~2400**
5	**Operating cost [2]**	**thousand-yuan /Y**	**6110**	**9340**	**8040**
	Raw material cost	thousand-yuan /Y	5550	6020	6020
	Electric changes	thousand-yuan /Y	180	2590	260
	Cost of steam	thousand-yuan /Y	200	160	1270
	Demineralized water fee	thousand-yuan /Y	-	10	10
	Maintenance costs	thousand-yuan /Y	180	560	480

Note：[1] Power consumption is the theoretical calculation value. Due to the operation mode and operation level is different. The actual statistics have deviation.

[2] Operation cost includes raw material costs, electricity changes, steam fee, demineralized water fee and the maintenance cost.The unit price of liquid ammonia is 3700 yuan/T. The unit price of urea is 2200 yuan/T. Electrovalency is 0.37yuan/ degree. Steam quality is 0.8MPa，200℃，Steam is 170 yuan/T.The demineralized water is 3 yuan/T. According to the value of static investment, the maintenance fee is 2%.

[3] The benchmark of three schemes is obtained according to the denitration reduction required dose of coal namely BMCR condition. The number of hours in yearly usage is at 5000 h.

[4] Urea hydrolysis according to four sets of two units of hydrolysis reactor.

4.Conclusions

In system security, carbamide is harmless to people and environment, while liquid ammonia is toxic and need to pass the safety evaluation to ensure the safety of the project. What's more, the influence feedback should include safety problem in public participation. As a result, when talking to safety, urea method is better than liquid ammonia process for caustic soda purification. When focusing on initial investment and operating cost, liquid ammonia process for caustic soda purification is the lowest, urea hydrolysis is the second,, urea pyrolysis is the highest. And from the perspective of system responsiveness to load respond of boiler, the fastest is liquid ammonia process for caustic soda purification; the second is urea pyrolysis; the slowest is catalyzes hydrolysis of urea.

In summary, in order to control the risk of safe operation in power plant effectively, it is suggested that urea method is more advantageous in densely populated area. In safe operation management with sufficient safeguards, liquid ammonia process is chosen under sparsely populated areas to save investment and operation cost.

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