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Experimental Study on Solid SCR Technology to Reduce NO_x Emissions from Diesel Engines

YINGSHUAI LIU [1,2] AND JIANWEI TAN [2]
[1]Weifang University of Science and Technology, Weifang 262700, China
[2]National Laboratory of Auto Performance and Emission Test, School of Mechanical and Vehicular Engineering, Beijing Institute of Technology, Beijing 100811, China

Corresponding author: Jianwei Tan (tanjianwei@bit.edu.cn)

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ABSTRACT To solve the problems of low exhaust temperature NO_x conversion efficiency of urea Selective Catalytic Reduction (SCR) and easy production of urea crystals during actual vehicle operation, this paper studies the effect of solid SCR on NO_x emission on the engine bench. The experimental results show that for a solid SCR carrying the same reducing agent, its volume is only 1/3 the volume of urea SCR. When the exhaust temperature is 160°C, the NO_x conversion efficiency of the solid SCR system can reach 40%. Based on the same ammonia-nitrogen ratio setting, the World Harmonized Steady Cycle (WHSC) NO_x conversion efficiency is improved by 3.3%, and the World Harmonized Transient Cycle (WHTC) NO_x conversion efficiency is increased by 4.5%. When the solid SCR injection temperature is reduced to 160°C, the NO_x conversion efficiency is significantly improved, which is 9.7% and 15.5% higher than that of the 200°C solid SCR system and the urea SCR system, respectively, and the number of power base windows is between [0 20]. The NO_x emission of diesel vehicles matching the urea SCR system is significantly higher, reaching 2.38 and 1.73 times that of the solid SCR system with a starting temperature of 160°C and 200°C, respectively.

INDEX TERMS Selective catalytic reduction, ammonia leakage, conversion efficiency, metal ammonia salt.

I. INTRODUCTION

As the number of vehicles in China increases each year, people are paying increasing attention to the sources of motor vehicle pollution. Among these vehicles, heavy diesel vehicles have a notably high contribution rate to such pollutants as PM2.5 and NO_x in atmospheric pollutants. Particulate matter (PM) emissions of heavy diesel vehicles account for 78% of total motor vehicle emissions, and NO_x emissions account for 57.3% of total motor vehicle emissions [1], [2]. Heavy-duty diesel vehicles are clearly the main contributors to motor vehicle pollution [3], [4].

To improve the air quality as soon as possible and win the blue sky defense battle according to the provisions of the China standard "GB17691-2018 vehicle compression ignition, gas fuel ignition engine and vehicle exhaust pollutant emission limits and measurement methods (China VI)" nationally, the implementation of the China VI-a and VI-b emission standards for heavy-duty diesel vehicles are set to begin on July 1, 2021 and July 1, 2023, respectively. To meet the emission requirements of China VI for diesel engines, aftertreatment devices commonly used at home and abroad are DOC-DPF-SCR, which are used to reduce NO_x and PM. Both aftertreatment technologies need to be used in combination to meet the China VI emission standards, but at present, there is still a large gap between research on engines and research on aftertreatment core technologies that meet the China VI emission standards [25]–[27].

In practical applications, the NO_x conversion efficiency of common low temperature SCR systems is not high. In particular, postal vehicles, buses, and sanitation vehicles running in cities need to be started and stopped frequently. Typically, the low exhaust temperature causes urea SCR systems to not operate normally [5]–[8]. In the China IV and China V emission standards, the average conversion efficiency of an SCR system needs to reach 75-85%. The SCR control strategy often uses an open loop control strategy based on the target conversion efficiency [9], [10]. In the China VI emission standards, the average conversion efficiency of the SCR system needs to be increased to 95-98%. To achieve such

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a high SCR conversion efficiency, it is often necessary to over-inject urea according to a certain proportion, and the risk of urea crystallization increases. How to reduce or avoid urea crystallization is a problem that urgently needs to be solved [11], [12]. Moreover, the China VI standard lowers the NH_3 leakage limit, and an ammonia trap ammonia slip catalyst (ASC) needs to be installed downstream of the SCR. In addition, when the exhaust temperature is higher than 380°C, the urea aqueous solution sprayed into the exhaust gas flow may be quickly dehydrated and transformed into melamine deposits, blocking the exhaust line, thereby resulting in increased engine back pressure, reduced power, and increased fuel consumption. These effects often occur inside and outside an engine [13].

Solid SCR technology is a new technology that has emerged in recent years for reducing NO_x emissions. A study by Figen *et al.* showed that solid SCR has higher NO_x conversion efficiency in the FTP72 and US06 test cycles [14]. Fulks *et al.* studied different types of solid ammonia and the ammonia release characteristics of storage materials [15]. Solid SCR technology carries ammonia with a volume density comparable to that of pure liquid ammonia. Under the same volume, the solid SCR technology can carry a more effective reducing agent than the urea SCR system. Research by Shost *et al.* shows that the advantage of solid SCR is that ammonia gas is directly injected into the exhaust pipe [16], which has greater NO_x emission reduction potential [5], [28], [29]. Solid SCR can solve the problems of current low temperature activity of urea SCR systems, exhaust pipe crystallization, and low temperature icing and is a highly promising NO_x emission control technology for diesel engines. This paper focuses on the NO_x emission reduction characteristics of solid SCR technology and compare it with urea SCR technology. The research results have reference significance for reducing the NO_x emissions of urban diesel vehicles in China and have a guiding significance for light diesel vehicles to meet the China VI emission standards [17]–[21].

II. INSTRUMENTS AND METHODS

A. INSTRUMENTS AND EXPERIMENTAL PLAN

The structure of the solid SCR system [22], [23] is shown in Figure 1. Solid SCR technology is used to store NH_3 in a closed container in the form of solid ammonia salt. The solid SCR system includes metal ammonia salt, an internal heater, a pressure reducing valve, a stainless steel tank, an aftertreatment control unit (ACU), a spray control valve, injection device, a pressure regulating valve, and an ammonia gas delivery pipe. The working principle of the system is that NH_3 is stored in the form of metal ammonia salt ($Sr(NH_3)_8Cl_2$) in a closed stainless steel tank. The metal ammonia salt is heated to a certain temperature, and ammonia gas will be released. The ACU receives the CAN communication signal of the ammonia nitrogen ratio of the engine controller ECU and injects NH_3 to the engine exhaust pipe in real time. Metal ammonium salt ($Sr(NH_3)_8Cl_2$) [24] is used as the storage

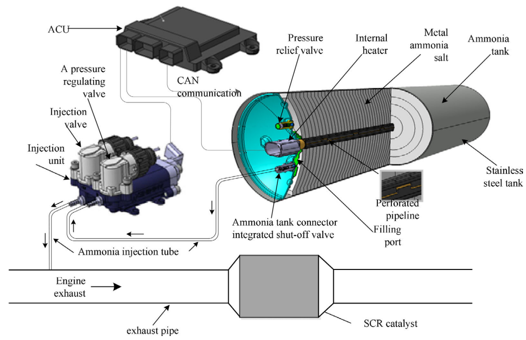

FIGURE 1. Schematic diagram of a solid SCR system.

medium for NH_3. This medium has the advantages of high ammonia storage efficiency and high low temperature activity. The NH_3 injection quantity is adjusted in real time according to different operating conditions of the diesel engine and chemically reacts with NO_x under action of the SCR catalyst to reduce the exhaust NO_x emissions of the diesel engine. For the NH_3 dose valve to accurately measure the NH_3 injection volume, the system monitors the pressure value of the closed container, and the temperature control unit performs closed loop control. Compared with urea SCR technology, solid SCR technology is not limited by the temperature of urea pyrolysis and hydrolysis, and there is no risk of urea crystals or urea stones blocking the exhaust pipe. Combined with a catalyst with good low temperature activity, it can effectively improve the low-temperature NO_x conversion efficiency of the SCR system and solve the problems of SCR systems in low-speed and low-load applications [30], [31].

The layout of the diesel engine bench is shown in Figure 2, including a dynamometer, emission test analyzer, a solid SCR system, a urea SCR system and an SCR catalyst. The catalyst adopts a copper-based catalyst or a vanadium-based catalyst with high conversion efficiency at low temperature. The main technical parameters of the diesel engine and aftertreatment are shown in Table 1. The main models and parameters of the test equipment are shown in Table 2. The specific parameters of the fuel used in the experiment are shown in Table 3. The control signal of the same ammonia nitrogen ratio of the solid SCR system and the urea SCR system is provided by the same controller on the engine test bench. The dynamometer is used to control the engine speed and torque based on the China VI emission standard. The WHSC and WHTC test cycle are used in the experiment, and the same diesel engine is tested with a solid SCR and a urea SCR injection system. Specifically, the gas sampling device directly samples the exhaust tail pipe of the aftertreatment system, the HORIBA exhaust gas analyzer is used to measure the NO_x pollutant emission results, and the environment SA ammonia gas analyzer is used to measure the amount of ammonia leakage.

B. INSTRUMENT AND EXPERIMENT PLAN

A supercharged and intercooled diesel engine was selected for a comparative study of NO_x reduction by solid SCR and

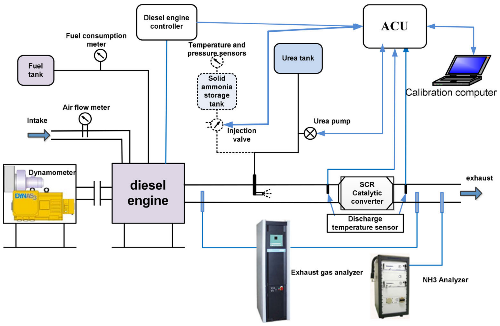

FIGURE 2. Diesel engine bench layout.

TABLE 1. Main technical parameters of the diesel engine and aftertreatment.

Parameter	Technical parameter
model	Four stroke and supercharged
Fuel supply form	High voltage common rail
Bore × stroke	80×130 /(mm×mm)
Rated power	220/ kW
Torque	1250/N.m
Maximum torque speed range	1200～1700 /r·(min)$^{-1}$
Turbocharger temperature limit	≤600℃
SCR catalytic converter	Φ266.7mm×304.8mm=17L

TABLE 2. Test equipment and manufacturer.

Model	Name	Manufacturer
ZAC450	Electric dynamometer	Xiangyi
AVL735	Fuel consumption	AVL
MEXA7500	Gas collection	HORIBA
FT-UV	Ammonia Analyzer	Environment S.A
Sensor flow	Intake air flow meter	ABB Ltd

urea SCR systems. First, the ammonia salt storage and release characteristics of the solid SCR are studied. Then, based on the same ammonia nitrogen ratio, the solid SCR adopts a passive injection mode. The passive urea injection receives the amount of reducing agent injection sent by the CAN bus and injects ammonia directly into the exhaust tail pipe. The reducing agent injected by the two systems is ensured to be the same, and WHSC and WHTC cycle test verifications are conducted. Laboratory test conditions, such as with a diesel engine, an intake system, an exhaust system, a cooling system, lubricating oil, fuel oil and an exhaust aftertreatment system, meet the national standard GB17691-2005 of the People's Republic of China. Experimental methods and test procedures include selecting WHSC and WHTC standard test cycles for comparative analysis experiments on the above two systems. According to the experimental requirements, the engine test bench records the working parameters of the

TABLE 3. Test fuel specific parameters.

Parameter	Value	Testing method
Sulfur content/×10^{-6}	10	GB/T19147-2016
Calorific value/MJ·kg^{-1}	42.77	GB/T 384-1988
Cetane number	51	GB/T19147-2016
density/20℃(kg·m^{-1})	841	GB/T19147-2016
Kinematic viscosity /20℃(mm^2·s^{-1})	4	GB/T19147-2016
Carbon content/%	86.0	SH/T 0656-1998
Hydrogen content/%	13.4	SH/T 0656-1998
Oxygen content/%	<0.2	ASTM D5622-95
Ash/‰	0.1	GB/T19147-2016

engine in real time, such as engine speed, torque, temperature, catalyst airspeed, ammonia nitrogen ratio and other parameters. The operating mode of each engine is stable for 3 minutes, and the data are recorded in the last 30 s. The exhaust component analyzer and the NH_3 analyzer are used to record the corresponding emission data.

Between the systems, 1 mol of urea can be hydrolyzed into 2 mol of ammonia, and the mass concentration of the urea standard aqueous solution is 32.5%; therefore, the relationship between solid SCR ammonia demand and urea demand is as follows equation:

$$Q_u = \frac{1}{2} \times \frac{M_u}{M_n} \div 32.5\% \times Q_n = 5.42 \times Q_n \tag{1}$$

In equation (1), Q_u is the urea demand, mg·s^{-1}; Q_n is the ammonia demand, mg·s^{-1}; M_u is the molar mass of urea, g·(mol)$^{-1}$; M_n is the molar mass of ammonia, g·(mol)$^{-1}$; the molar masses of ammonia and urea are 17 g·(mol)$^{-1}$ and 60 g·(mol)$^{-1}$, respectively.

The surface temperature of the SCR catalytic converter is replaced by the arithmetic mean of the inlet and outlet temperatures of the converter. The conversion efficiency of the SCR catalytic converter is shown in equation (2), where η_N represents the NO_x conversion efficiency of the catalytic converter;C_{Nin} represents the NO_x concentration at the inlet of the catalytic converter; C_{Nout} represents the NO_x concentration at the outlet of the catalytic converter.

$$e_{gas} = \frac{m}{W\left(t_{2,i}\right) - W\left(t_{1,i}\right)} \tag{2}$$

Error analysis uses the standard deviation equation (3) [32]–[34]. Where σ is the standard deviation, N is the total number of samples, i is the sample serial number, Xi is the value of the sample, and μ is the arithmetic mean.

$$\sigma = \sqrt{\frac{1}{N} \sum\nolimits_{i-1}^{N} (x_i - \mu)^2} \tag{3}$$

TABLE 4. Ammonia storage density of different reductant.

Reducing Agent	Molar Mass/mol	Density g/cm³	Quality /g	Volume /cm³
Liquid Ammonia	17	0.6	0.6	0.9
Solid SCR	60	1.3	1.0	0.8
Adblue	---	1.1	3.1	2.8
$Sr(NH_3)_8Cl_2$	294.5	1.3	1.2	1.0

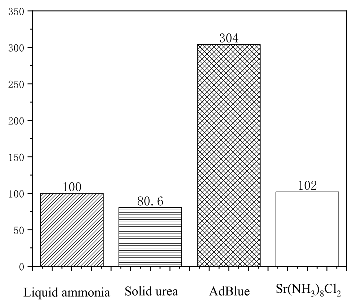

FIGURE 3. Different reductant volume ratio.

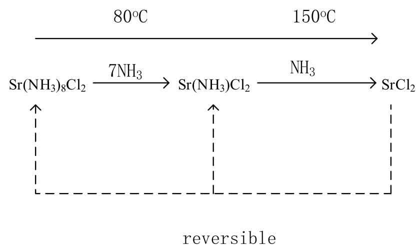

FIGURE 4. Ammonia adsorption desorption reaction of $SrCl_2$.

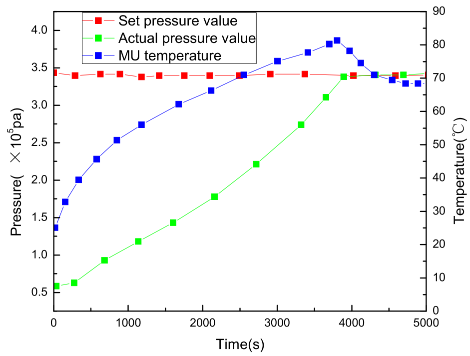

FIGURE 5. Temperature/pressure characteristics of MU during system warm-up.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. COMPARISON OF STORAGE DENSITY OF A SOLID SCR AND A UREA SCR

The main reaction of the SCR system to reduce the NO_x emissions of diesel engines is as follows: $4NO+4NH_3+O_2 = 4N_2+6H_2O$, 1 g NO=1/30 mol the amount of reducing agent required to reduce 1 g NO by several different ammonia storage media (NSR=1). The volume ratio of pure liquid ammonia, solid SCR, AdBlue and solid ammonia storage material $Sr(NH_3)_8Cl_2$ required to reduce the unit mass of NO is 0.93:0.75:2.83:0.95. The volume of pure urea ammonia is the reference volume 100, and the volume of each reducing agent is shown in, for example, Figure 3. Among the reducing agents required to reduce the mass of NO, solid SCR has the smallest volume and AdBlue has the largest volume. $Sr(NH_3)_8Cl_2$ has the same volume as pure liquid ammonia. $Sr(NH_3)_8Cl_2$ has a volume of approximately 1/3 of AdBlue. It can be seen that the solid SCR system can carry a more effective reducing agent than the urea SCR system under the same storage volume. Therefore, the cruising range of the solid SCR system carrying the same quality reducing agent is higher than that of the urea SCR system. The application of a solid SCR system can greatly reduce the system volume and is more conducive to the layout of the whole vehicle.

B. COMPARISON OF A SOLID SCR AND A UREA SCR BENCH TEST

As shown in Figure 4, the release characteristics of the solid SCR system NH_3 changes with temperature. When the solid SCR stainless steel tank is heated to the threshold temperature, only metal ammonia salts can release stored NH_3. The chemical equations (4) and (5) of strontium chloride metal ammonia salt ($Sr(NH_3)_8Cl_2$) releasing ammonia gas are as follows:

$$Sr(NH_3)8cl2 \overset{80°C}{\longleftrightarrow} Sr(NH_3)cl2 + 7NH_3 \tag{4}$$

$$Sr(NH_3)cl2 \overset{150°C}{\longleftrightarrow} Srcl2 + NH_3 \tag{5}$$

According to the characteristics of the above reaction, NH_3 can be stored in a closed container in the form of solid ammonia compound in advance, and the temperature of the closed container can be controlled by the system control unit to release the NH_3 adsorbed by the metal ammonium salt in the form of gas and sealed in a closed In the container, NH_3 is then quantitatively injected into the exhaust gas flow according to the requirements of the diesel engine operating conditions, and a reduction reaction occurs with NO_x, thereby achieving the purpose of controlling NO_x emissions.

According to the storage and release principle of the NH_3 in a solid SCR system, as shown in Figure 4, when the temperature reaches 35°C, $Sr(NH_3)_8Cl_2$ begins to release the stored NH_3, and when the temperature reaches 80°C, $Sr(NH_3)_8Cl_2$ releases the stored Seven NH_3 molecules release the last NH_3 at 150°C. The experiment studied the ammonia release characteristics during the preheating process of the solid SCR system as shown in Figure 5.

At normal temperature, the residual gaseous NH_3 in meter unit (MU) can be gradually adsorbed by strontium chloride ($SrCl_2$) to form metal ammonium, which reduces the pressure of MU and forms a negative pressure, as shown in Figure 5. When the solid SCR is working, the ACU controls the heater

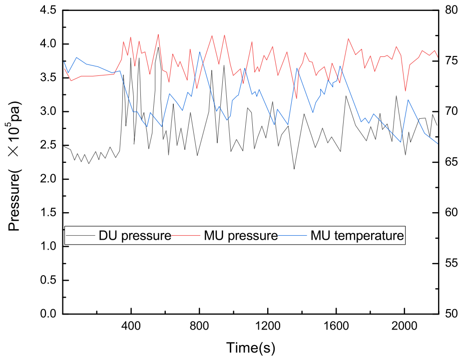

FIGURE 6. Temperature/pressure characteristics of MU during transient cycling.

to heat the solid ammonium salt stored in the MU; therefore, the temperature of the main tank MU increases, and the metal ammonium salt gradually releases the adsorbed NH_3 under heating to increase the MU pressure. The ACU controls the NH_3 release rate of the metal ammonium salt by changing the heating power of the heater, thereby controlling the actual pressure of the MU to the pressure value set by the system. In the solid SCR system, the system working pressure is set at 3.4×10^5pa. The injection unit (DU) is connected to the MU through the NH_3 delivery pipe. During the preheating process of the solid SCR system, the DU pressure regulating valve is intermittently opened, and the NH_3 generated in the MU enters the DU injection chamber through the pressure regulating valve; therefore, the DU pressure also gradually increases. When the actual pressure value of the MU reaches the system set pressure value, the DU pressure also reaches the system set pressure value. At this time, the solid SCR system ends the preheating process and enters the standby state. The preheating time of the MU system depends on the heating power of the heater.

During the test, the solid SCR system MU set the working pressure to 3.4×10^5pa. After the engine is started, the engine is warmed up. At the same time, the MU enters the warm-up state. After the MU warms up to the set working pressure, the solid SCR system enters the normal working state. The solid SCR system is controlled by the ACU to spray the reducing agent NH_3. The dynamometer is adjusted to run the engine at rated operating conditions for 10 minutes. After the engine operating parameters and catalyst temperature are stable, the WHTC cycle is entered directly. As seen from Figure 6, when the engine is running stably at the rated operating point, the DU pressure tends to stabilize at approximately 2.2×10^5pa, which proves that the DU continues to inject the reducing agent NH_3 at a large flow rate at this time, and the main tank temperature and pressure gradually stabilize at 75°C and approximately 3.3×10^5pa. When entering the WHTC transient cycle, the pressure of the DU rises rapidly, indicating that the injection volume of the DU is reduced, causing the pressure of the main tank to rise. At this time, the ACU reduces the heating power of the main tank, and the temperature of the main tank decreases. Then, the release rate of the solid ammonium salt NH_3 decreases, and the main tank pressure is reduced. With the continuous injection of NH_3, the pressure of the main tank gradually decreases. When the pressure of MU is lower than the set pressure value, ACU increases the heating power of the main tank, causing the temperature of MU to rise. The release rate of NH_3 of $Sr(NH_3)_8Cl_2$ increases, thus increasing the main tank pressure. It can be seen from Figure 6 that the ACU adjusts the temperature of the main tank according to the pressure signal value of the main tank, thereby controlling the NH_3 release rate of $Sr(NH_3)_8Cl_2$. The temperature and pressure of the MU are always under dynamic control of the ACU. When the average injection amount of reducing agent NH_3 is 30.5 mg·s^{-1} under WHTC transient cycle conditions, the average pressure of MU of the solid SCR system is 3.51×10^5pa, and the average temperature of MU is 70.9°C.

The NH_3 released by the main tank MU enters the injection unit DU through the DU ammonia inlet, and the pressure of the injection chamber is adjusted by the pressure adjustment solenoid valve. The ACU calculates the reducing agent NH_3 injection duty cycle according to the engine operating conditions and the temperature and pressure of the NH_3 in the injection cavity. The injection solenoid valve injects the reducing agent NH_3 into the exhaust pipe according to the ACU duty cycle signal to achieve the reducing agent NH_3 quantitative injection. The experiment investigated the DU pressure response characteristics of the solid SCR system under WHTC transient cycling conditions, as shown in Figure 7.

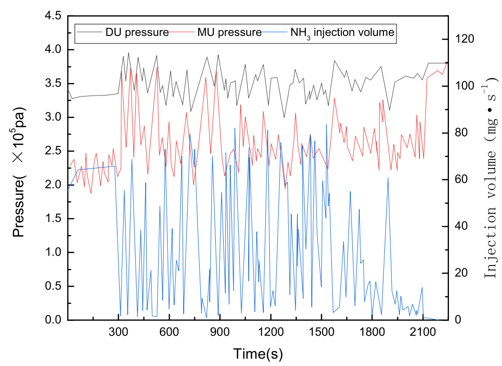

FIGURE 7. Pressure response characteristics of injection unit DU.

During the test, the solid SCR system MU set the working pressure to 3.4×10^5pa. After the engine is started, the engine is warmed up, and at the same time, the MU enters the warm-up state. After the MU warms up to the set working pressure, the solid SCR system enters the normal working state. The solid SCR system is controlled by the ACU to perform normal injection. After adjusting the engine to rated operating conditions for 10 minutes, the WHTC cycle is entered to test the DU response performance of the solid SCR system.

When the NH_3 released from the main tank MU enters the DU through the ammonia inlet, the injection solenoid valve of the DU is closed, and the pressure adjustment solenoid valve is intermittently opened. The NH_3 enters the DU injection chamber through the pressure adjustment solenoid valve, causing the DU pressure to rise. During DU injection, the ACU calculates the NH_3 injection pulse width according to the DU pressure, temperature and nozzle flow characteristics. At this time, the pressure adjustment solenoid valve is closed, the injection solenoid valve is opened, and the NH_3 in the DU injection chamber is injected into the exhaust pipe through the injection solenoid valve. The pressure in the injection chamber is reduced. Due to the small volume of the DU injection chamber, the DU pressure changes considerably during the solid SCR operation. As seen from Figure 8, the DU pressure depends on the MU pressure and the DU injection amount. When the DU injection amount changes greatly, the DU pressure changes are more drastic; when the DU injection quantity changes less, the MU and DU pressures change less and gradually stabilize.

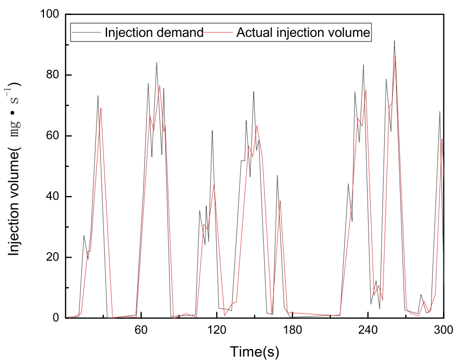

FIGURE 8. Injection unit DU response characteristics.

The experiment investigated the injection response characteristics of the solid SCR system under WHTC transient cycling conditions. When the DU is injected, the ACU calculates the basic NH_3 injection amount based on the NO_x concentration upstream of the catalyst and the exhaust gas flow rate. Based on the basic injection amount, the reductant injection amount is corrected according to the catalyst temperature, airspeed MAP, and transient correction factor, and the reductant is finally determined. The ACU calculates the opening pulse width of the injection solenoid valve based on the DU pressure signal and nozzle flow characteristics, and the reducing agent NH_3 in the DU injection chamber is injected into the exhaust pipe through the injection solenoid valve. Due to the opening and closing of the DU pressure regulating valve and the injection solenoid, the NH_3 pressure in the injection chamber is in a fluctuating state, resulting in a certain difference and lag between the actual injection amount of the solid SCR system and the injection demand during the work process, as shown in Figure 8.

It can be seen from the middle diagram that the solid SCR system actual injection amount of reductant has a good response characteristic. During the 300s working time, the total injection requirement of the system is 6.686 g, and the actual injection amount is 6.596 g; the injection accuracy rate is 98.65%, has good injection volume response characteristics, there is a 2s lag time between the actual injection volume and the injection demand.

Figure 9 shows a comparison of NO_x conversion efficiency of the solid SCR and the urea SCR at different exhaust temperatures of 30000 hr^{-1} airspeed. The ammonia-nitrogen ratio is set to 1:1 by ACU. The experimental results show that when the exhaust temperature is lower than 250°C, the conversion efficiency of the solid SCR is significantly higher than that of the urea SCR. Between the systems, at 160°C, NO_x conversion efficiency increased by 40%, at 180°CNO_x conversion efficiency increased by 40%, at 200°CNO_x conversion efficiency increased by 35%, and at 220°CNO_x conversion efficiency increased by 25%. The NO_x conversion rate of the urea SCR at low temperature is mainly limited by the temperature of urea pyrolysis and hydrolysis, resulting in low conversion efficiency at low temperature. In the range of 300°C to 400°C, the NO_x conversion efficiency of the solid SCR system is equivalent to the urea SCR, and the highest conversion efficiency is close to 95%. In this temperature range, the catalyst activity is the best and the highest NO_x conversion efficiency is achieved. Experimental results show that when the exhaust gas temperature is lower than 200°C, the solid SCR ammonia leakage is significantly higher than that of the urea SCR. The main reason is that the urea aqueous solution injected into the exhaust pipe cannot be completely hydrolyzed into ammonia gas. Solid SCR injects ammonia directly into the tail pipe. When the exhaust temperature is higher than 200°C, the urea hydrolysis efficiency is higher; therefore, the ammonia leakage is equivalent to that of the solid SCR.

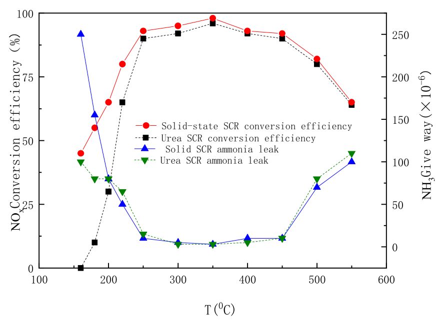

FIGURE 9. SCR conversion efficiency and ammonia leakage.

As shown in Figure 10, the NO_x emissions of the WHSC diesel engine without aftertreatment is 9.25 g·(kW·h)$^{-1}$. The same ammonia nitrogen ratio is set as in the WHSC cycle, and a solid SCR and urea SCR comparative test is conducted separately. The test results show the NO_x emissions are reduced to 1.65 g·(kW·h)$^{-1}$ and 1.95 g·(kW·h)$^{-1}$, the average NH_3 leakage is 1.2×10^{-6} and 1.7×10^{-6}, and the ammonia escape peaks are 6×10^{-6} and 8×10^{-6}, respectively. The average NO_x conversion efficiency was 82.2% and 78.9%, respectively. The conversion efficiency of the solid SCR is improved by 3.3%, and the difference in ammonia leakage is small.

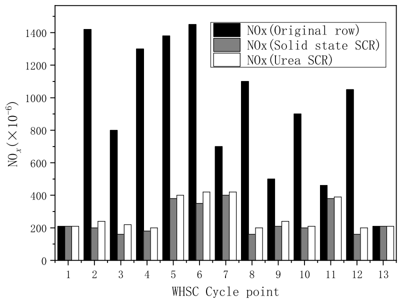

FIGURE 10. **WHSC NO_x conversion efficiency.**

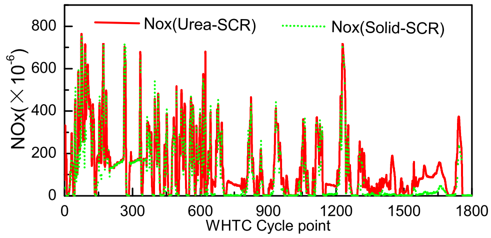

FIGURE 11. **Comparison of NO_x Conversion efficiency based on WHTC cycle.**

As shown in Figure 11, the NO_x emissions of the diesel engine without aftertreatment WHTC bare metal is 8.99 g·(kW·h)$^{-1}$. The same ammonia nitrogen ratio is set as in the WHTC cycle, and comparative test of solid SCR and urea SCR is conducted. The test results show that the NO_x emissions are reduced to 1.5g·(kW·h)$^{-1}$ and 1.9g·(kW·h)$^{-1}$. The peaks of ammonia leakage occurred at 78×10^{-6} and 55×10^{-6}, respectively. The average ammonia leakage was 4.3×10^{-6} and 3.0×10^{-6}, respectively. The average NO_x conversion efficiency is 83.3% and 78.8%, respectively, and the NO_x conversion efficiency of the solid SCR system is increased by 4.5%. These results occur because the WHTC cycle is switched to the high speed section from 1400 to 1600s, the load of the diesel engine suddenly increases, and the exhaust flow rate quickly increases. At this time, the ammonia storage capacity in the SCR tank is large, the temperature of the SCR tank rises rapidly, and the ammonia storage capacity drops to cause the ammonia gas to overflow. Due to the strong storage capacity of the copper-based SCR catalyst, ammonia leakage is likely to occur when the temperature of the SCR catalyst suddenly increases.

C. AMMONIA STORAGE CHARACTERISTICS OF THE SOLID SCR SYSTEM

Figure 12 shows the dynamic response characteristics of the SCR catalyst at a 200°C exhaust temperature and 25000hr^{-1} airspeed. The ammonia storage maximum experiment needs to remove the ASC. During the experiment, the upstream and downstream temperatures of the SCR catalyst and the upstream and downstream NO_x concentrations are recorded including the downstream NH_3 concentration, urea injection quantity, engine intake air quantity, fuel injection quantity and other related parameters. The engine runs at the rated point

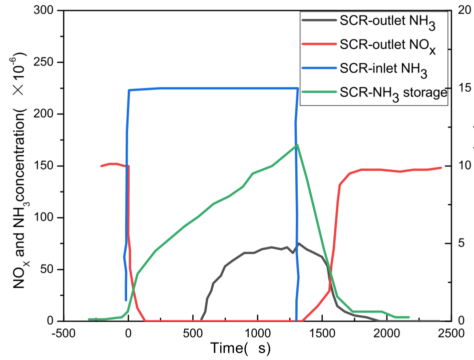

FIGURE 12. **SCR ammonia storage characteristics.**

for 10 to 15 minutes and stops the urea injection to empty the ammonia storage in the SCR catalyst. The engine operating conditions are manually adjusted to operating conditions with the SCR average temperature of 200°C and the airspeed of 25000 hr^{-1}. After the temperature before and after the SCR and the upstream and downstream NO_x concentrations are stable, data recording begins. When the ammonia nitrogen ratio was adjusted to 1.3 to inject urea, the downstream NO_x concentration dropped rapidly, the ammonia storage amount gradually increased, and NH_3 leakage began to rise slowly at 400 s When NH_3 leakage rose to 70×10^{-6}, urea injection was stopped. When the downstream NO_x concentration rapidly rises to the original diesel engine emission concentration, the data recording is stopped. According to the data from the start of urea injection until the NH_3 leak reaches 25×10^{-6}, according to the dynamic chemical balance of the SCR catalyst, $NH3_{in}$ is the NH_3 mass flow into the catalyst, NO_{xin} enters the catalyst NO_x mass flow, and $NH3_{out}$ is The NH_3 mass flow rate overflows the catalyst and the NO_{xout} exhaust NO_x mass flow rate of the catalyst. The accumulated difference after integration is the maximum ammonia storage amount corresponding to the operating point. To meet the China VI emission regulations, the NO_x average efficiency needs to reach more than 95%. Generally, Copper-based catalysts with better low temperature conversion efficiency are selected. Copper-based catalysts have a higher storage capacity at low temperatures. The ammonia storage of the SCR catalyst decreases as the temperature of the catalyst increases, and at the same temperature point, as the storage amount increases, the NO_x conversion efficiency increases.

D. COMPARISON OF SOLID SCR AND UREA SCR VEHICLE ROAD EXPERIMENTS

During the on board test, the test route is divided into three parts, urban roads, suburban roads, and highways, according to such factors as maximum speed of the test vehicle, road traffic intensity, and road intersection density distribution, as shown in Table 5.

Figure 13 illustrates is a comparison of NO_x conversion efficiency of the solid SCR and the urea SCR with the change of vehicle speed. It can be seen from the figure that as

TABLE 5. Vehicle test route composition.

Road type	Top speed ($km \cdot h^{-1}$)	Road length (km)	Proportion
Urban road	40	13.3	49.6%
Suburban road	60	10.2	38.1%
Highway	90	3.3	12.3%

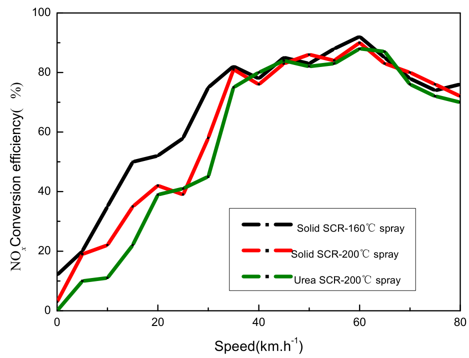

FIGURE 13. Comparison of NO_x conversion efficiency between the solid SCR and the urea SCR.

the vehicle speed increases, the engine workload gradually rises and the exhaust gas temperature gradually increases; furthermore, the corresponding NO_x conversion efficiency also increases simultaneously. The solid SCR directly injects ammonia into the exhaust tailpipe; therefore, there is no risk of urea crystallization. The starting temperature of solid SCR urea is adjusted to 160°C for injection. The vehicle speed is in the range of 0-40 $km \cdot h^{-1}$, and the NO_x conversion efficiency is significantly improved. Compared with 200°C, the solid SCR system and urea SCR system have increased by 9.7% and 15.5%. In the range of vehicle speeds >40 $km \cdot h^{-1}$, while maintaining the same ammonia nitrogen ratio, the conversion efficiency is equivalent. Thus, for urban diesel vehicles that have been operating at low speeds for a long time, using solid SCR technology and reducing the injection temperature can effectively improve the NO_x conversion efficiency of pollutants.

The power-based window method divides the experimental results into several window data subsets suitable for evaluating the performance of PEMS. The size of the power base window is the WHTC cycle power of the engine, and the average specific emission value of all sampling points in the power base window is calculated. The movement of the power base window is 1 s, and the process mainly includes a work-based window method and a CO_2-based window method. The period of the average window $(t_{2,i} - t_{1,i})$ is determined by equation (6), as follows:

$$W(t_{2,i}) - W(t_{1,i}) \geq W_{ref} \quad (6)$$

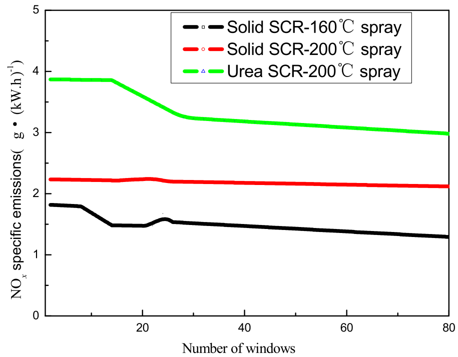

FIGURE 14. Comparison of NO_x conversion efficiency between the solid SCR and the urea SCR with vehicle speed.

$W_{(t_{j,i})}$ is the engine cycle work from start to time $t_{j,i}$, kW.h; W_{ref} is the cycle work of WHTC, kW.h; $t_{2,i}$,, as shows in the following equation (7):

$$W(t_{2,i} - \Delta t) - W(t_{1,i}) < W_{ref} \leq W(t_{2,i}) - W(t_{1,i}) \quad (7)$$

Δt is the data sampling period, which is less than or equal to 1 s. Equation (8) is used to calculate of the emission of each window and each pollutant as follows:

$$e_{gas} = \frac{m}{W(t_{2,i}) - W(t_{1,i})} \quad (8)$$

m is the emission quality of each pollutant in $mg \cdot window^{-1}$; $(W_{2,i} - W_{1,i})$ is the engine cycle power of the i-th average window, the average power of the effective window is greater than 20% of the maximum power of the engine, and the effective window ratio is at least 50%.

Figure 14 shows a comparison of the NO_x specific emissions of solid SCR and urea SCR based on the power-based window method. As seen from the figure, the number of power-based windows is between [0 20], and the NO_x emissions of diesel vehicles matching the urea SCR system are significantly higher. The results are 2.38 and 1.73 times that of the solid SCR system at 160°C and 200°C, respectively. The urea SCR pollutant NO_x is significantly higher than the solid SCR system. The main reason is that urea needs to be hydrolyzed after injection into the exhaust tail pipe. Pyrolysis can produce reducing agent ammonia gas. If the car is run for a short period of time, its exhaust temperature has not reached the appropriate hydrolysis pyrolysis conditions, and its reducing agent generation rate is low. Therefore, for vehicles that start and stop frequently, the SCR pollutant NO_x is relatively high in the initial stage.

IV. CONCLUSION

In this paper, the effects of solid SCR and urea SCR on diesel NO_x emissions are studied on an engine bench. The main conclusions are as follows:

(1) The solid SCR system can carry more effective reducing agent than the urea SCR system, which is only 1/3 of the standard urea aqueous solution. This amount helps to

facilitate the installation and layout of the entire vehicle and achieve light weight.

(2) The solid SCR directly injects ammonia gas into the exhaust pipe, which has a lower light off temperature and can improve the NO_x conversion efficiency at low temperatures. In the WHSC and WHTC cycles, the solid SCR system has a higher NO_x conversion efficiency than the urea SCR system as 3.3% and 4.5%, respectively. The ammonia storage of the SCR catalyst decreases as the temperature of the catalyst increases, and at the same temperature point, as the storage amount increases, the NO_x conversion efficiency increases.

(3) For diesel vehicles in the city that have been operating at low speeds for a long period of time, using solid SCR technology and lowering the injection temperature can effectively improve the NO_x conversion efficiency of pollutants. When the vehicle speed is in the range of 0-40 $km\cdot h^{-1}$, the solid SCR injection temperature is reduced to 160°C, and the NO_x conversion efficiency is significantly improved, which is 9.7% and 15.5% higher than that of 200°C in the solid SCR system and the urea SCR system. The number of power based windows is between [0 20], and the NO_x emissions of diesel vehicles matching the urea SCR system are significantly higher at 2.38 and 1.73 times that of the solid SCR system with injection at 160°C and 200°C, respectively. The future work needs to do experimental parameter optimization on solid SCR technology by using artificial intelligence technology [35], [36].

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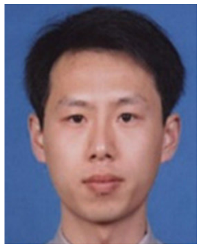
YINGSHUAI LIU received the B.S. degree in optical information science and technology, and the M.S. degree in optical engineering from the Ocean University of China, Qingdao, China, in 2005 and 2009, respectively, and the Ph.D. degree in power machinery and engineering from the Beijing University of Technology, Beijing, China, in 2019.

He is currently a Lecturer with the Weifang University of Science and Technology. He is also engaged in Postdoctoral Research by joint training with Southwest Jiaotong University and Ningbo Free Trade Zone. His research interests include engine energy saving and emission reduction and green manufacturing, green logistics and transportation, intelligent inspection and repair of automotive, decision making and intelligent optimization, facility location, and prediction and assessment for economic and environment. He has published over ten journal and conference proceedings papers in the above research areas, including the IEEE Transactions on Automation Science and Engineering, *Computers & Chemical Engineering*, and *Computers & Industrial Engineering*.



JIANWEI TAN received the B.S. degree in computer and applications from the Ocean University of China, Qingdao, China in 2001, and the M.S. degree in power machinery and engineering, and the Ph.D. degree in environmental engineering from the Beijing Institute of Technology (BIT), Beijing, China in 2004 and 2007, respectively. From 2012 to 2013, he was a Visiting Scholar with Cornell University. He joined BIT, in 2007, where he is currently an Associate Professor of internal combustion engine engineering. He is the Evaluation Expert of the National Natural Science Foundation of China. He is a Motor Vehicle Review Expert from the Beijing Eco-Environmental Bureau. He has over 90 publications. His research interests include vehicle emission, sensor networks, big data, transportation, and energy systems.