

Studies on the effectiveness of SCR catalysts during combustion of pulverized coal

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Abstract. The motivation of this paper is new NO_x emission regulations according to IED Directive 2010/75/EU of EU which introduce the BAT's conclusions as binding. The paper presents the methodology and results of research on the effectiveness of SCR catalysts during combustion of pulverised coal in a model furnace installed at the Institute of Power Engineering and Turbomachinery of the Silesian University of Technology (IPET). The aim of the research was to search for catalysts that could be placed in a regenerative rotary air heater - RAH-SCR. Two catalysts were tested: a commercial plate-type based on V₂O₅ and a prototype ceramic based on platinum. Presented results of investigation demonstrate a potentially high efficiency of RAH-SCR installations which can meet new environmental regulations of NO_x emission. The highest NO_x reduction efficiency (92.87%) was obtained for an industrial catalyst at 329°C, from about 436.3 to 31.1 mg/m³ as NO₂ @ 6%O₂ to 31,1. At lower temperature, 260°C maximum efficiency of NO_x reduction does not exceed 60%, from 440,0 to 169,6 mg/m³. The placement of the catalyst in the RAH can also be a support for SNCR installations due to the increase in DeNO_x efficiency and reduction of NH₃ slip.

1 Introduction

New law regulations according to IED Directive [1] establish BAT (Best Available Techniques) for large combustion plants (thermal input 50MW or more). The respective decision [2] has been published 31 July 2017, and these requirements will become effective in mid-2021. In terms of NO_x emissions, this corresponds to the following levels (Table 1).

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Table 1. NO₂ emission standards of BAT conclusions

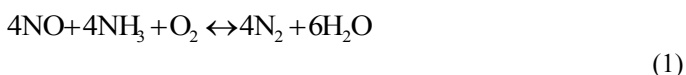
Parameter	Unit	Current limit	BAT conclusions	
			Existing plants	New plants
NO ₂ limit	mg/m _a ³ @ 6% O ₂	200	65-150* <85-200**	65-85* 80-125**

* annual average; ** daily average

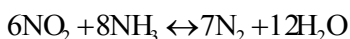
The SCR technology is practically one which can meet the new regulations. The development of SCR technology is essential for the power industry. In the case of SCR, there are many references describing the current state of the art [3, 4, 5].

The reagent is injected into the flue gas duct in front of the catalyst. The result is the conversion of nitrogen oxides NO_x to the surface of the catalyst, most often at a temperature between 300°C - 400°C in the presence of oxygen contained in the flue gas:

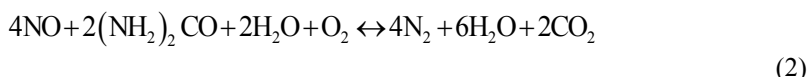
- if the reducing agent is ammonia, then:



or



- if the reducing agent is urea, thus



or



Because of health and safety rules for transport and storage, the most used is aqueous ammonia. An important argument against the introduction of urea solution into the convection part of the boiler is its corrosiveness. Condensed ammonia (liquid form) must be converted into a gaseous form. In industrial application solution of aqueous ammonia is evaporated on temperature 180 – 250 °C and is mixed with compressed air; after that gaseous mixture is injected into spraying nozzles. The appropriate mixing of the reactant with flue gas is also necessary to obtain efficient NO_x reduction [6, 7].

To minimize the NH₃ slip, the optimal ratio NH₃/NO_x must be maintained [3, 8, 9]. Maximal dose of NH₃ and achieved NO_x reduction is determined by catalyst characteristic, its geometry and shape, porosity and thus active catalyst surface and gas residence time [5]. However many factors could decrease reduction effect such as: fouling and formation of ABS (ammonium bisulphate), ammonia chlorides and other species, adsorption and absorption of NH₃ on fly ash, catalyst corrosion and erosion and blockage of catalyst active centres and its deactivation by heavy metals mainly arsenic and alkali metals (Na, K).

2 Methodology

In this study SCR experiments were carried out on Drop Tube Reactor (DTR) equipped and adapted for SCR tests. A significant advantage of this installation is high flexibility and the simplicity of controlling the process parameters that imitate the work of SCR an industrial installation. In Fig. 1. experimental facility is presented. The reactor is electrically heated heat-resistant and acid-resistant stainless steel tube with an inner diameter 300 mm. Reactor is equipped with pulverised fuel burner, fuel and air supply system, data acquisition and control system. The catalyst is placed in a specially prepared SCR section. SCR section is

equipped with a 3 stage static mixer providing proper mixing ammonia with the flue gas, before the catalyst. Ammonia dosing system is fitted with high-quality spraying nozzle. To increase the flue gas and reagent mixing efficiency, the mix of ammonia with neutral gas N₂ is applied. The lab SCR installation has a wide control range of Area Velocity (depend on the type of catalysts) and of NH₃/NO ratio 0-6.

Investigated fuel was the hard coal from the Polish mine KWK Sobieski. Fuel represents typical coal utilized in the Polish power sector. It is characterized by high Lower Heating Value Q_{d1} = 27.24 MJ/kg and high volatiles content V^{daf} = 41.76% enabling easy ignition. Ultimate, proximate, ash oxides and ash fusibility analyses, and heavy metals content were investigated in a certified laboratory. The results of the analysis are presented in Table 2. For proper burnout in DTR hard coal were milled to cumulative percentage retained R_{0.2} ≤ 1%.

Table 2. Basic analysis of coal

Ash oxides analysis	SiO ₂ (%)	CaO (%)	K ₂ O (%)	P ₂ O ₅ (%)	Al ₂ O ₃ (%)	MgO (%)	Fe ₂ O ₃ (%)
	53.4	2.52	2.51	0.16	24.3	1.53	8.48
	SO ₃ (%)	Na ₂ O (%)	TiO ₂ (%)	Cl (%)	BaO (%)	SrO (%)	Mn ₃ O ₄ (%)
	2.36	2.70	0.89	-	0.08	0.04	0.04
Ultimate analysis of fuel	C ^d (%)	H ^d (%)	S ^d (%)	N ^d (%)	Cl ^d (%)	O ^d (%)	Q _{d1} (MJ/kg)
	74.71	3.15	0.86	1.07	0.146	10.36	27.24
Proximate analysis of fuel	W ^r (%)	A ^d (%)	V ^{daf} (%)				
	2.6	9.7	41.76				
Ash fusibility temperature red./oxy.	IDT (°C)	ST (°C)	HT (°C)	FT (°C)			
	1150/1250	1210/1280	1240/1350	1310/1400			
Heavy metals content in fuel	Hg, mg/kg	As, mg/kg					
	0.116	2.16					

Two catalysts were investigated. The first (marked as KX) was vanadium (V₂O₅) catalyst from resources of IPET – Fig. 2a. This is a plate type catalyst often used in SCR installations. The second (marked KP) is a prototype platinum catalyst on a ceramic carrier – Fig. 2b.

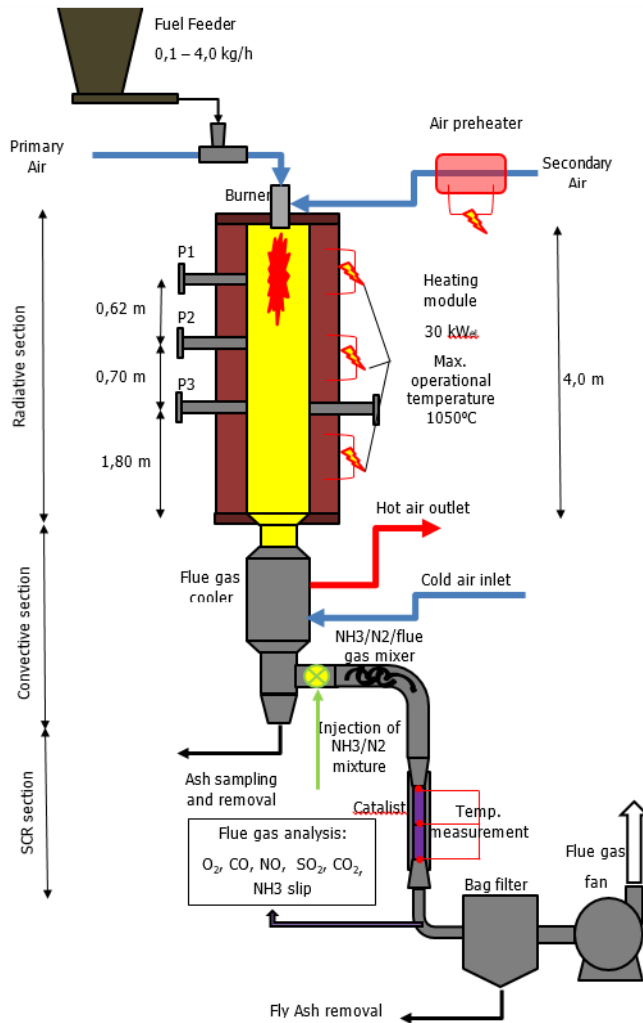


Fig 1. Drop Tube reactor equipped with SCR facility.

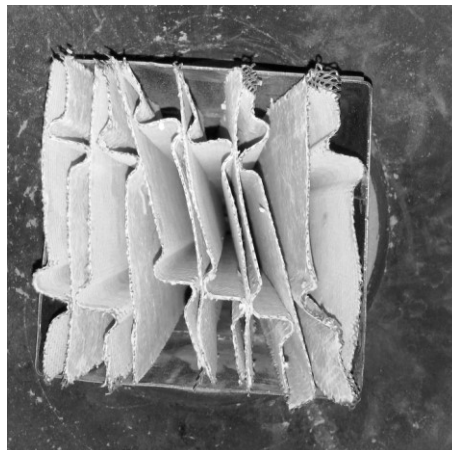


Fig 2a. Catalysts KX installed to lab SCR section



Fig 2b. Catalysts KP installed to lab SCR section

3 Results and discussion

3.1 Catalyst KX

The results of tests at various temperatures are presented in in Fig. 3 – 6. Additionally, the area velocity AV [m_n/h] value, defined as the quotient of the flue gas stream [m³_n/h] and the contact surface of the catalyst [m²], was determined.

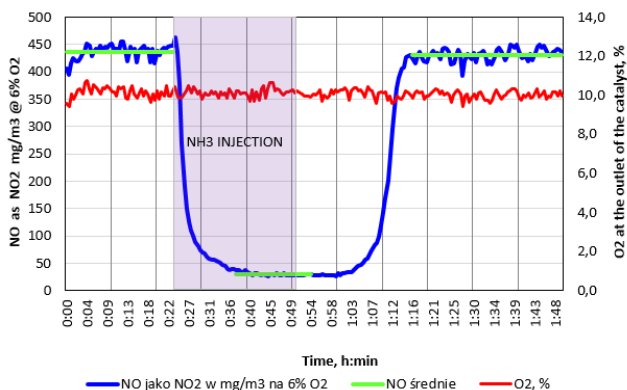


Fig 3. Concentration of NO (as NO₂ @ 6% O₂) and O₂ during tests of the KX catalyst temperature 329°C.

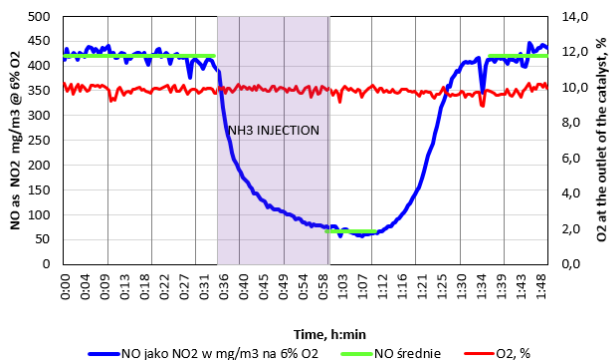


Fig 4. Concentration of NO (as NO₂ @ 6% O₂) and O₂ during tests of the KX catalyst temperature 290°C.

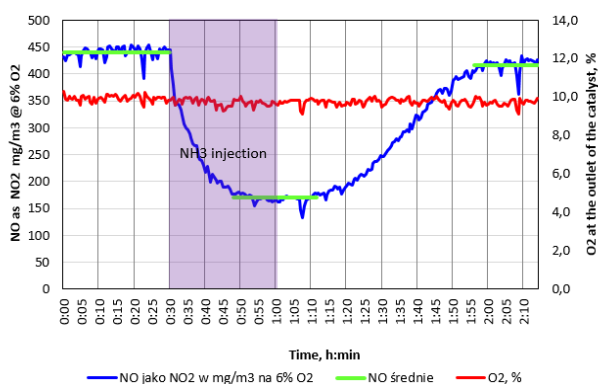


Fig 5. Concentration of NO (as NO₂ @ 6% O₂) and O₂ during tests of the KX catalyst temperature 262°C.

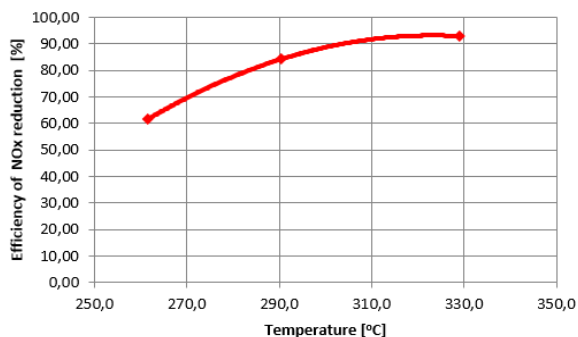


Fig. 6 Efficiency of the KX catalyst versus temperature for 50 ml_{NH3}/min.

The AV values were between 6.97 - 7.22 m_n/h, what is slightly below the standard for the industrial catalysts according to [8, 10]. It should be mentioned that with increased AV the efficiency of NO_x reduction η_{NO_x} is lower. The tests for the NH₃ stream 300 ml_{NH3}/min and 50 ml_{NH3}/min showed similar results.

3.2 Catalyst KP

The results of tests at various temperatures are presented in Fig 7. The upper (red) curve corresponds to the NH_3 stream of 300 $\text{ml}_{\text{NH}_3}/\text{min}$ while the lower (blue) curve to the NH_3 stream of 50 $\text{ml}_{\text{NH}_3}/\text{min}$.

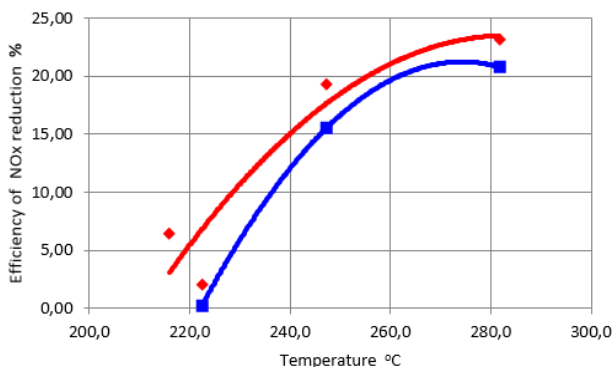


Fig 7. Efficiency of the KP catalyst vs. temperature: red - 300 $\text{ml}_{\text{NH}_3}/\text{min}$, blue 50 $\text{ml}_{\text{NH}_3}/\text{min}$.

The AV calculated for the tests were between 13.06 - 15.4 m_n/h . These values are in the standard for the industrial catalysts according to [8, 10]. Compared with KX with lower AV, such an increase in AV may be responsible for lowering the NOx reduction efficiency η_{NO_x} by about a dozen percentage points [8, 10]. Further decrease of η_{NO_x} was probably caused by the fly ash fouling of the surface of the KP catalyst.

4 Conclusions

- The maximum efficiency of NOx reduction obtained for the KX catalyst was $\eta_{\text{NO}_x} \cong 92,87 \%$, for the temperature 329 °C.
- After lowering the temperature to 260 °C the efficiency was still relatively high and exceeded 60%.
- The KX catalyst shows a strong relationship between efficiency and temperature. This imposes the need to ensure proper flue gas temperatures in the area of its operation. This significantly limits the thickness of the catalytic layer if it is placed on the hot end of the RAH in boilers.
- The results of measurements of the prototype ceramic KP catalyst show its low efficiency, not exceeding $\eta_{\text{NO}_x} \cong 23 \%$. This is probably due to its sensitivity to fly ash fouling. Such a catalyst was more effective in a test conducted for natural gas combustion gases [9].

Given the above, further research should focus on the study of commercial catalysts that provide high levels of η_{NO_x} . However, it is necessary to test the suitability of such catalysts for use in RAH. They must then meet two basic conditions:

- adequate mechanical strength in operating conditions as a heating element for the mobile RAH rotor,
- the ability to transfer the appropriate heat flux in the preheater.

Such tests can be carried out only on the model ROPP or on the real object in industry.

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