



Experimental investigations of ammonia adsorption and nitric oxide reduction on activated coke

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ABSTRACT

In this work the enhancement of ammonia adsorption on activated coke has been investigated to increase the efficiency of the denitrification in the dry flue gas cleaning system located at Infraserv GmbH & Co. Hoechst KG in Frankfurt am Main, Germany. The influence of loading temperatures and sulfur components content of the activated coke on the ammonia adsorption were studied. Additionally, urea was tested as an alternative loading substance. Increasing ammonia adsorption was observed by raising loading temperatures. The highest ammonia loading was possible at the highest temperature tested at 469 °C. The activated coke loaded at these conditions, as well as the one loaded with urea, was found to have higher denitrification efficiency than that loaded at present conditions of about 114 °C. The results of this study allowed the recommendation of possible measures to be applied in the plant to increase its denitrification efficiency.

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1. Introduction

The combustion of coal in power plants results in the formation of undesired air pollutants among which the nitrogen and sulfur oxides are the most important. The flue gases released from coal combustion can be cleaned by different means that have been classified into wet, semi-dry and dry systems. A simultaneous desulfurization and denitrification dry flue gas cleaning system using activated coke as an adsorbent/catalyst is available. The first systems working under these characteristics were installed in the 1980s in Matsushima, Japan and Arzberg, Germany. Currently, this secondary measure for flue gas treatment has an important application in Asia.

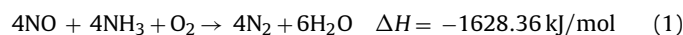
One of these dry flue gas cleaning systems is installed at the Industrial Park Hoechst in Frankfurt am Main, Germany, and operated by Infraserv Hoechst to treat the flue gases produced by the combined heat and power plant mainly fueled with coal. The flue gas cleaning system was originally designed and constructed by the Bergbau–Forschung–Udde alliance in 1989. The initial process was designed to work under the principles of a selective catalytic reactor (SCR) for the reduction of nitric oxides with ammonia using activated coke as a catalyst. This was achieved by the injection of ammonia into the flue gas just before the entrance to the denitrification stage, inside the activated coke adsorber. Due to the

clogging of the equipment caused by the formation of ammonium chloride, originated from the reaction of the injected ammonia and the hydrochloric acid contained in the flue gas, the system had to be modified. Now, the reduction of the nitric oxides emission to the allowed limits is achieved only by the implementation of primary measures in the combustion. This way, the formation of the nitric oxides is prevented. Additionally, the ammonia injection was changed in position to perform a pre-loading of the activated coke before it enters the adsorption unit.

The current situation of the plant shows a high percentage of ammonia losses in the system. To solve this, different tests on the ammonia adsorption were done to optimize the procedure. The optimization of the ammonia injection will, in turn, increase the denitrification efficiency and reduce the losses in the system. It is not only important to increase the amount of ammonia on the surface of the activated coke but also that this ammonia is available for nitrogen oxides reduction.

The ammonia adsorption was tested with different sulfur contents of the activated coke and with different loading temperatures. Some samples of activated coke were also loaded with urea, as an alternative ammonia loading substance. Activated cokes pre-loaded with ammonia or urea were tested for denitrification efficiencies.

The denitrification process works by the reaction of the nitric oxides contained in the flue gas with the adsorbed ammonia on the surface of the activated coke, as stated in Eq. (1).



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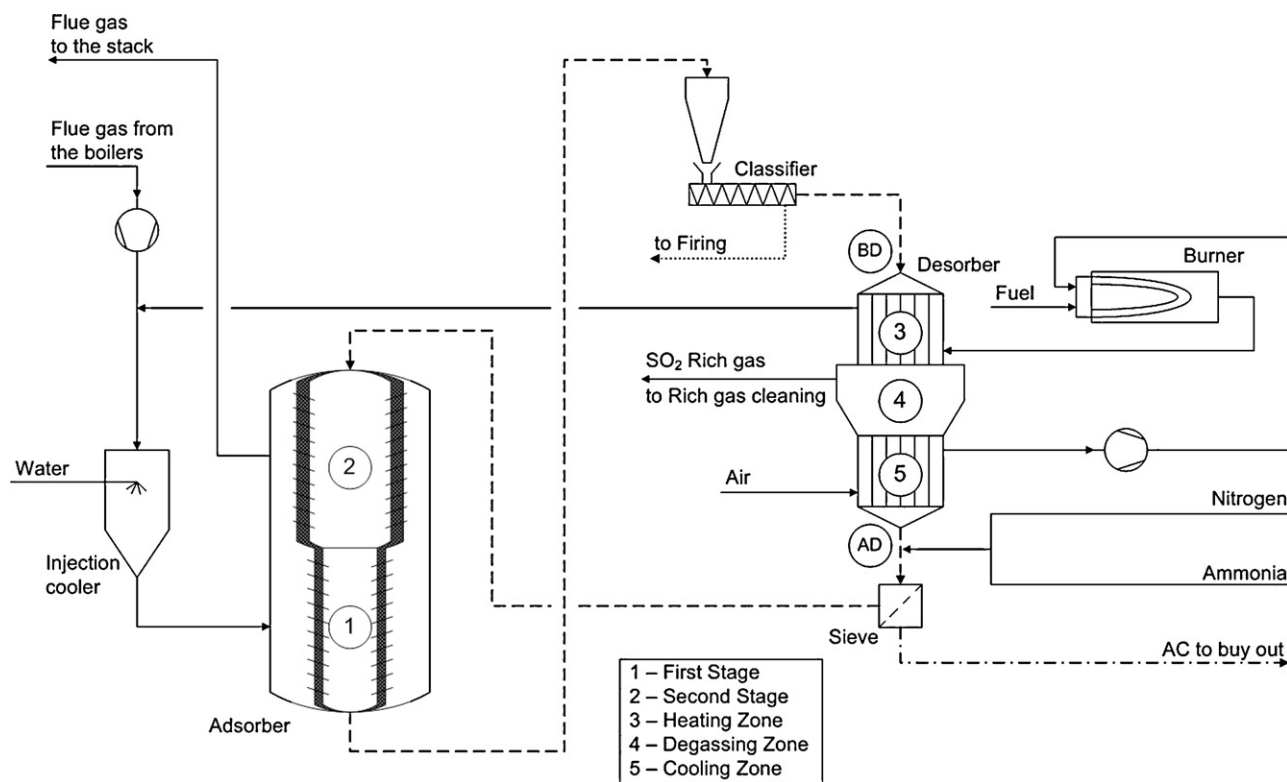


Fig. 1. Bergbau-Forschung-Uhde process scheme.

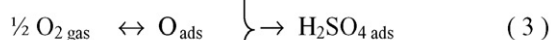
This equation represents the reaction on the surface of the activated coke. Due to the modifications in the system at Infraseriv Hoechst the denitrification tests are guided to determine the efficiency of activated cokes that have been previously loaded with ammonia. These denitrification tests involve no ammonia injection in the gas phase. In any case, the ammonia must first be adsorbed on the activated coke and then it becomes available for the reaction with the nitric oxide [1]. Therefore, the chemical system simulated in these tests is the same. There is no previous reference in the literature in which the denitrification system has been tested under these conditions, where the activated coke is first loaded with ammonia (110–470 °C) and then tested for the NO conversion efficiency with no additional ammonia injection. Only activated cokes used to evaluate the ammonia treatment efficiencies have had procedures in which the activated coke is first set in contact with the ammonia and then brought into the denitrification [2]. Nonetheless, the functioning principles of this theory are related to the presence of nitrogen reducing groups on the surface of the activated coke and not to the amount of ammonia loaded and also not related to the breakthrough times of ammonia adsorption.

2. Bergbau-Forschung-Uhde flue gas cleaning process

The Bergbau-Forschung-Uhde (BF/Uhde) process is a dry process for flue gas cleaning with activated coke as adsorbent/catalyst. It is used for simultaneous NO_x conversion and SO₂ removal. The BF/Uhde system is located in the cold end of the flue gas stream, after the air pre-heater and the electrostatic precipitator. The process consists of three sections: the adsorption, desorption and rich gas cleaning. The Bergbau-Forschung-Uhde process scheme installed in the power plant of Infraseriv Hoechst is shown in Fig. 1.

The adsorption is done in two stages in an activated coke adsorber unit, where the simultaneous desulphurization/denitrification process can be guided, as well as the reduction of other air toxics and dust. The activated coke is continuously moving downwards.

In the first stage, the majority of the SO₂ removal takes place. Sulfur dioxide, together with water vapor and oxygen, is adsorbed in the form of sulfuric acid, Eqs. (2)–(4).



The sulfur trioxide can also be separated in processes of flue gas cleaning with activated coke by reacting with water to form sulfuric acid, as shown in Eq. (5), and then be adsorbed on the activated coke [3].



In the second (upper) stage of the adsorber unit, the activated coke is used as a catalyst that enables the reduction of the NO_x molecules. In the original process, the ammonia was injected into the flue gas between the first and second stage. At the plant of Infraseriv Hoechst, this ammonia injection does not exist.

The activated coke loaded with SO₂ and discharged from the adsorber unit is transported to the top of the desorption section. The desorber unit is divided into three zones, the heating (upper), the degassing (middle) and the cooling (lower) zone. In the heating zone, flue gas is used to heat up indirectly the activated coke to a temperature of 400–450 °C, which corresponds to the required desorption temperature for SO₂. The heated activated coke enters then the degassing zone which has a bigger volume than the other zones, to ensure a higher residence time of the activated coke. The main desorbed component is SO₂. Here, the rich gas is concentrated and leaves the desorber unit towards the rich gas cleaning section.

In the cooling zone the temperature of the activated coke is lowered by the indirect contact with the cooling gas. A cooling to about

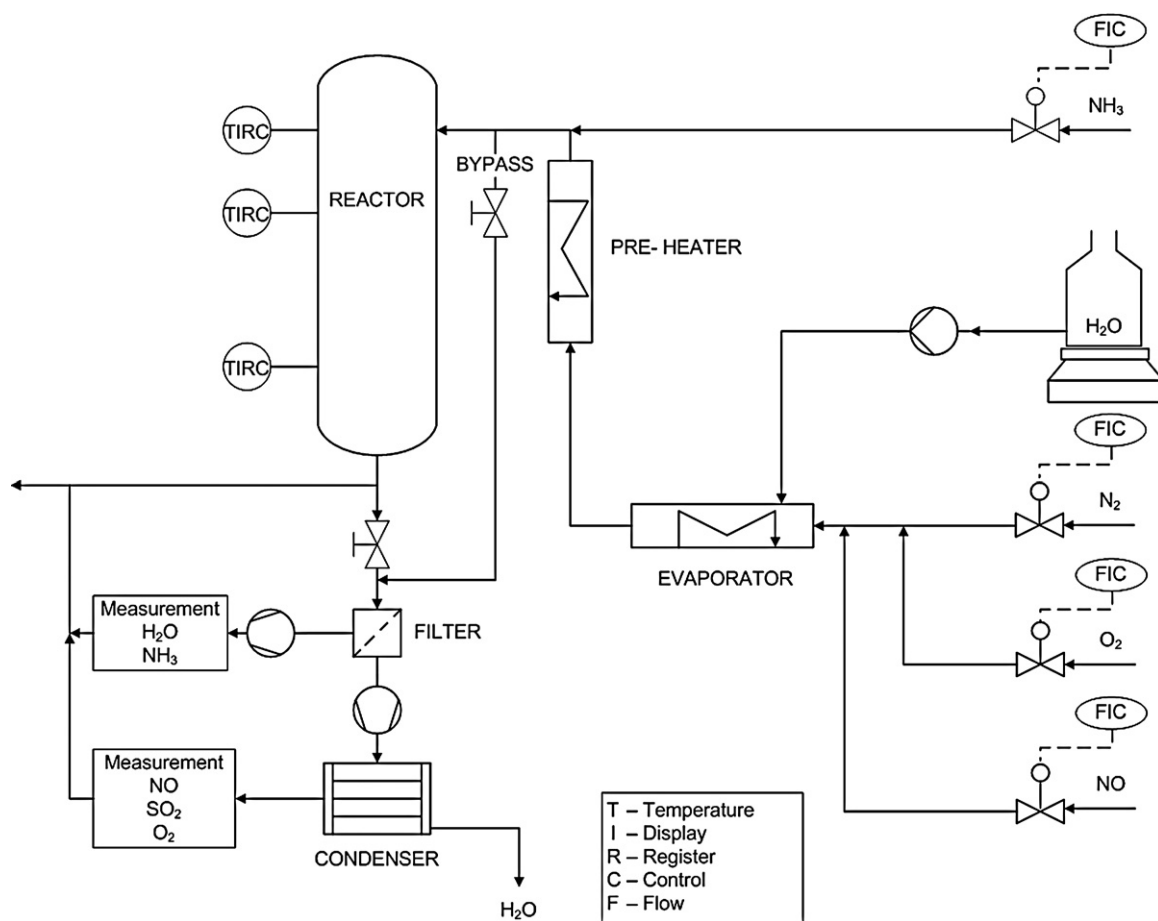


Fig. 2. Laboratory scale test plant for activated coke.

100 °C is achieved. The activated coke exiting the desorber unit can be fed back into the adsorber unit.

3. Ammonia adsorption enhancement

The adsorption can be divided in two types: physisorption and chemisorption. The physisorption is a physical adsorption in which the intermolecular forces attract the adsorbate (in this case ammonia) to the adsorbent (activated coke). This type of adsorption decreases with the increase in temperature. On the other hand, adsorption can also occur in a chemical way, which involves an electron transfer forming a real chemical bond between the adsorbate and the adsorbent [4]. The relation of this type of adsorption with the temperature change is highly dependant on the conditions and nature of both the adsorbate and adsorbent.

The chemisorption of ammonia on activated coke results in the formation of different nitrogen-containing functional groups on the surface of the solid that enhances the reduction of acidic pollutants, like the nitric oxides. These effects have been previously studied by several authors [5–11] and are compiled in the ammonia treatment concept. The ammonia treatment can be defined as a treatment of carbon based adsorbents under an ammonia atmosphere. In literature [5–11], the treatment is done at temperatures between 200 and 800 °C for a fixed length of time, between 10 min and 3 h. Additionally, some authors have pointed out that the reduction efficiencies of treated carbon based adsorbents towards the pollutants can be increased with increasing treatment temperatures and times [5–7].

The reduction of NO by the use of NH₃, on activated coke has been described by several authors. Kleinschmidt [1] presented a

schematic description of the NO reduction on activated carbon in the presence of ammonia, in which three different paths to reduce the pollutant are described. The paths show that the reduction of NO is done by the reaction with ammonia in an adsorbed state. This conclusion has been confirmed by Gálvez [12]. Nevertheless, these studies were tested under SCR conditions. In the present study it is assumed that this reaction will take place under the same principles if the ammonia is first adsorbed on the activated coke and then brought into contact with the NO.

An additional effect of the ammonia adsorption has been tested and referenced by other authors [2,9,10,13]. The ammonia adsorbed on activated coke results in the formation of reducing sites, i.e. formation of nitrogen-containing functional groups on the surface of carbonaceous adsorbents like activated coke. In the practice [9], the ammonia treatment at high temperatures results in the “non-SCR” reaction occurring between the NO and the activated coke containing these types of functional groups. Miyagawa and Miya [14] report an increase in the reduction efficiency of about 10% by a NO concentration of 100 ppm.

4. The laboratory scale testing plant

The laboratory scale tests were done in a plant containing a fixed bed stainless steel reactor.

The plant offers the possibility of mixing the following gases, using N₂ as carrier gas: NO, O₂, H₂O_{vap} and NH₃. Measurements of the inlet gas volume flows and exit flue gas concentrations of these components are available. The testing plant is sketched in Fig. 2.

The NO, O₂, N₂ and NH₃ are brought into the system directly as gases. The H₂O enters the system initially as liquid and is vaporized

Table 1
Measurement equipment for flue gases of the test plant.

Parameter	Principle	Name of the equipment	Scale
NO	Infrared photometer	NGA/2000 Rosemount	0–1000 ppm vol
NO ₂	Ultraviolet photometer		0–50 ppm vol
SO ₂	Ultraviolet photometer		0–2500 ppm vol
NH ₃	Infrared photometer	Binos Rosemount/Leybold Heraeus	0–1000 ppm vol
H ₂ O	Infrared photometer		0–30 vol%
O ₂	Paramagnetic	Magnos 5G Hartmann Braun	0–25 vol%

in the evaporator. NO, O₂ and N₂ enter the evaporator together with the H₂O. The NH₃ inlet is directly before the reactor.

The gas mixture can be heated in the pre-heater. There is a three point temperature measurement available in the reactor. From these, the middle temperature was used as the reference.

The total capacity of the reactor is of about 1.3 dm³. The diameter of the reactor is 52 mm (base area of 2124 mm²) and the maximum height of the activated coke in the reactor was 499 mm.

At the exit of the reactor, a filter protects the measuring equipment from any possible particulate matter exiting with the flue gas and a condenser traps the water of the flue gas. The measurement equipment for the test plant composition, its principles and characteristics are listed in Table 1.

5. Experimental procedure

In the dry flue gas cleaning plant, the ammonia loading and denitrification occur in different positions and conditions. In order to fit best the experiments to the conditions of the dry flue gas cleaning system installed at the plant at Infracorv Hoechst, the tests were divided into two big groups: loading tests and denitrification tests.

5.1. Types and parameters of the used activated coke

Two samples of activated coke of about 30 dm³ each, one before and one after the desorber, were extracted from the flue gas cleaning plant of Infracorv Hoechst. Fig. 1 shows the sampling positions: “BD” before desorber and “AD” after desorber. The sample before desorber (BD) is coming from the adsorber unit, where a reduction of SO₂ is achieved by its adsorption on the surface of the activated coke, as stated in Eqs. (1)–(4). Therefore, the sample BD has a high sulfur content. The sample after desorber (AD) has a low content of sulfur components because they are desorbed mainly as SO₂

Table 2
Results from the analysis of the activated cokes.

Parameter	Unit	Activated coke before desorber	Activated coke after desorber	Activated coke VA5
Compacted bulk density	kg/m ³	586	530	600
Bulk density	kg/m ³	629	561	–
Particle density	kg/m ³	1660	1830	2100
BET surface area	m ² /g	355	475	550
H ₂ SO ₄ content	mass%	4.53	0.09	0
Sieve analysis				
>5.00 mm	mass%	6.7	4.6	42.3
5.00–4.00 mm	mass%	75.5	68.2	55.8
4.00–3.36 mm	mass%	8.4	10.3	1.2
3.36–2.80 mm	mass%	4.1	5.8	0.4
2.80–1.00 mm	mass%	3.1	6.4	0.1
1.00–0.50 mm	mass%	0.2	0.2	–
<0.50 mm	mass%	2.0	4.5	0.2
Water	mass%	0.9	0.5	–
Ash	mass%	13.4	14.3	–
Carbon	mass%	66.3	71.5	92.2 (a.w.f.)
Hydrogen	mass%	2.1	1.9	0.7 (a.w.f.)
Nitrogen	mass%	1.9	2.1	0.6 (a.w.f.)
Sulfur	mass%	3.3	1.7	0.5 (a.w.f.)
Oxygen	mass%	12.1	8.0	2.9 (a.w.f.)
Volatile matter	mass%	19.9	15.0	–

a.w.f.—ash and water free.

during the regeneration of the activated coke in the desorber unit. Parameters tested on these samples are listed in Table 2.

The content of sulfuric acid (H₂SO₄) on the surface of the activated coke samples before and after desorber was determined in the laboratory as a reference of the sulfur content, because this compound is said to be the last of the catalytic reactions occurring to SO₂ in the adsorption process [3]. The H₂SO₄ content of the activated coke sample after desorber is only 0.09%, while the content in the sample before desorber is 4.53% (Table 2).

To represent a point in between the sampling points, an activated coke sample (ABD) composed of 50 vol% of activated carbon before desorber and 50 vol% of activated coke after desorber was produced. This sample is called the 50/50 sample.

The fresh adsorbent which is brought into the flue gas cleaning system of the power plant is activated coke type VA5 from CarboTech AC GmbH in Essen, Germany (Table 2).

5.2. Ammonia loading

The ammonia loading tests were focused on the ammonia adsorption on the activated coke. The variables tested for the ammonia loading were:

- The sulfur components content of the activated coke, dependent on the sampling point, as explained before: activated coke before desorber BD with high sulfur components content, activated coke after desorber AD with low sulfur components content and of 50/50 percent in volume of these two.
- The loading temperatures. Temperatures were varied from about 114 °C, current loading temperature in the plant, to 469 °C, for a high temperature loading.

Table 3
Volume and mass flows for denitrification tests.

Volume flow in working conditions	2160	dm ³ /h (STP)		
Volume flow in STP conditions	1257	dm ³ /h (STP)		
Temperature	130	°C		
Parameter	Concentration	Unit	Flow	
NO	124	ppm vol dry	181.5	cm ³ /h (STP)
O ₂	6.4	vol% dry	93.7	dm ³ /h (STP)
N ₂	82.6	vol% dry	1208.5	dm ³ /h (STP)
H ₂ O	11	vol%	2.2	g/min
NH ₃	0	vol% dry	0	dm ³ /h (STP)

The loading experiments were done on samples with a volume of 1.06 dm³. The reactor was initially filled with 0.96 dm³. On top of it a sampling mesh containing the rest 0.1 dm³ was located. The sampling mesh was used to extract samples after loading. The filled reactor was then heated to the desired loading temperatures. The loading of ammonia was achieved by leading a mixture of nitrogen and ammonia gas (3.8 vol%) flow through the bed. The exit ammonia concentration was controlled. The breakthrough time, time it takes the exit ammonia concentration to change from 0, was registered. This time was then used to calculate the percentage ammonia mass load by using the ammonia inlet volume flows, as expressed in Eq. (6).

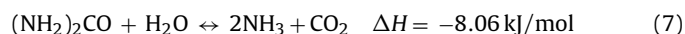
$$m_{\text{NH}_3\text{Load}} = \frac{\dot{V}_{\text{NH}_3} t \rho_{\text{NH}_3}}{m_{\text{sample}}} 100 \quad (6)$$

with $m_{\text{NH}_3\text{Load}}$ = ammonia load in %mass, \dot{V}_{NH_3} = volume flow of ammonia in the system in dm³/h (STP), t = breakthrough time in (h), ρ_{NH_3} = ammonia gas density (0.7714 dm³/g), m_{sample} = mass of the activated coke sample in g.

Each sample remained in the reactor for additional 10 min after the breakthrough time to ensure a complete saturation of the whole bed profile. After this time the ammonia loading tests were finished and the sampling mesh extracted. For the cases in which the loading was followed by denitrification test, the rest of the activated coke was left inside the reactor, or else the reactor was emptied. An exception was done with the loading test at 469 °C; given that the loading temperature was much higher than the denitrification test temperature, in this case the activated coke was extracted after loading, cooled down and poured back for the denitrification test. Therefore, the possibility of desorption of ammonia during cooling down was reduced.

5.3. Loading with urea

The urea was used as an alternative ammonia loading substance. According to literature one mole of urea will dissociate into 2 mol of ammonia, see Eq. (7), starting at temperatures of 133 °C [15].



The urea was loaded by spraying it as a solution on the activated coke, while continuously manual stirring. Two different solution concentrations were prepared to achieve 0.4 and 1 mass% ammonia load equivalents. Calculations according to Eq. (7) were done to determine the required concentrations in these solutions. This loading was performed at room temperature.

5.4. Procedure for denitrification test

Denitrification tests were designed to simulate the conditions under which the catalyzed nitric oxide reduction on pre-loaded activated coke occurs under real process conditions. The gas conditions for these tests were set according to those found at the entrance of the denitrification (second) stage of the adsorber in the

plant: temperature around 130 °C and concentrations of the main flue gas components entering the stage (nitric oxide, water and oxygen) according to the measurements done directly in between the desulfurization (initial) stage and the denitrification stage, shown in Table 3.

The reactor, containing 0.96 dm³ of pre-loaded activated coke (with ammonia or urea), was heated to the desired denitrification temperature of approximately 130 °C, at the middle of the reactor. For the case of the blank, denitrification without loading, no pre-loading was required.

The nitrogen was flowing during the whole time. The water and oxygen flows were opened as soon as the exit temperature had reached 100 °C (to avoid water condensation inside the reactor). Finally, once the temperature in the middle point had reached approximately 130 °C, the nitric oxide valve was opened and the test time started. The efficiency of removal of pollutants is commonly referred in literature by the ratio c/c_0 , where c is the exiting concentration and c_0 the inlet concentration, of the pollutant. The inlet concentration of NO was in these tests not possible to be measured, because the equipment was installed downstream of the reactor. An initial inlet concentration with an empty reactor was set on 124 ppm vol and the equipment was calibrated at this concentration. Nevertheless, during the denitrification tests this inlet concentration was susceptible to change. The tests were carried out for a total time between 18 and 20 h. From the results, it was observed that most of the tests had reached their highest NO exit concentration 300 min (5 h) after the test was started. For this reason the concentration after 300 min (c_{300}) was used instead of the inlet concentration (c_0) to determine the efficiency by the ratio c/c_{300} . This adaptation shall ensure the comparability of the results between the different tests.

5.5. Test coding

In order to simplify the reference to the tests done, a code was designed. The code contains the following information, in the same order:

- type of tests (*L* for loading and *D* for denitrification),
- type of activated coke tested (BD for before desorber, AD for after desorber and ABD for the 50/50 volume mixture of these two) and
- the loading substance and temperature, for the case of ammonia, or loading substance and equivalent ammonia load, for the case of urea.

As an example, L-BD-NH3-116 is a loading test, done with before desorber activated coke, with ammonia at a temperature of 116 °C. For the case of the denitrification without loading the last part of the code is not applicable and is therefore referred to as D-AD-00.

5.6. Kjeldahl-Nitrogen measurement

The Kjeldahl-Nitrogen measurement is a quantitative method of determination for the nitrogen content. In this method the sample

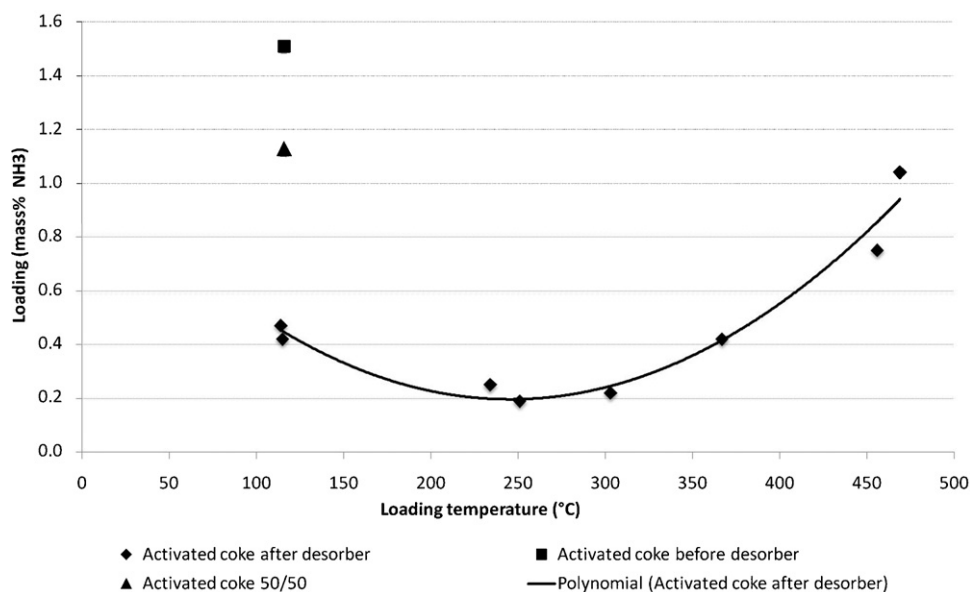


Fig. 3. Ammonia load on activated coke at breakthrough time.

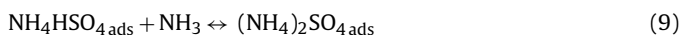
is heated with sulfuric acid. The organic substances are decomposed by oxidation and the nitrogen is reduced to ammonium sulfate. Then, the solution is distilled and the amount of nitrogen can be determined by titration. The Kjeldahl-Nitrogen content is the sum of ammonium nitrogen, ammonia and organical bounded nitrogen. The samples were tested under this method to specify the amount of nitrogen on them and its increase or decrease after treatment with ammonia as a reference to determine the amount of ammonia physisorbed or chemisorbed. The Kjeldahl-Nitrogen test was used as a reference and it was required in order to verify the results calculated from the loading tests.

6. Results and discussion

6.1. Ammonia adsorption enhancement

The ammonia load optimization opportunities were tested with reference to the ammonia adsorption capacities using three variables: the sulfur content of the activated coke (dependent on the sampling point), the loading temperature and the loading substance. The amount of ammonia adsorbed was determined in two ways. One was by using the ammonia breakthrough times to calculate the mass% load. The second was by the determination of the Kjeldahl-Nitrogen content in the samples after loading tests.

The results of the ammonia adsorption tests are shown in Fig. 3. This figure expresses the influence of both the sulfur contents and the loading temperatures on the maximum ammonia mass loads at the breakthrough time. According to these results, a higher content of sulfur compounds in the sample increases the ammonia load on the activated coke at about 114 °C. This increase results from ammonia on the activated coke. The SO₂ of the flue gas is adsorbed as sulfuric acid (H₂SO₄) as shown in Eqs. (2)–(5). The sulfuric acid on the surface of the activated coke can react with the ammonia to form ammonium salts, Eq. (8). The formed species can further react with ammonia as shown in Eq. (9).



Therefore, a higher sulfuric acid content in a sample could cause a higher consumption of ammonia.

Regarding the effect of the temperature on the ammonia loading, the results show a variable influence. Between 114 and 250 °C the ammonia load decreased with increasing loading temperatures. On the other hand, above 250 °C the load is increased with the temperature raise. A similar type of variable behavior, with ranges of positive and negative temperature effects on adsorption, have also been found for other types of adsorbates and adsorbents [16]. This condition was explained by means of two types of adsorption processes. The decreasing ammonia load until 250 °C is caused by a dominant physisorption. A similar result was obtained by Rodriguez [17] on studies done for the ammonia adsorption on a fixed bed of activated carbon for temperatures between 40 and 120 °C. It was shown that the ammonia breakthrough time was smaller with increasing temperatures at this range.

For temperatures above 250 °C the chemisorption, energy activated process, is dominant and enhances this way the adsorption. As a result, for the activated coke loaded at different temperatures, the highest ammonia load is obtained at 469 °C (highest tested temperatures) as shown in Fig. 3.

For temperatures above the 230 °C, a sulfur dioxide content in the flue gas of the testing plant was identified, meaning that desorption of the sulfur compounds took place. Due to the possibility of the ammonia to react with these, there could be a related influence on the ammonia uptake. The quantification of this influence is yet to be determined.

The ammonia loading causes either the physisorption or chemisorption of ammonia. In the first case, ammonia would be found as a component and in the second case new nitrogen functional groups will be formed, as stated by the ammonia treatment principles [5–11]. The determination of the Kjeldahl-Nitrogen contents of the samples, done in laboratory, was used to account for the total ammonia and nitrogen compounds contained in the samples. All of this as a way of confirming the results obtained by the calculation of the ammonia percentage mass loads using the breakthrough times. The results for these determinations are shown in Fig. 4.

The lowest value in this graph corresponds to the Kjeldahl-Nitrogen contained in the activated coke without loading. It is not possible that this content corresponds to the amount of ammonia on the surface as no loading was applied. Nevertheless, this content of nitrogen can be explained by the original ammonium nitrogen and the organical bounded nitrogen of the activated coke.

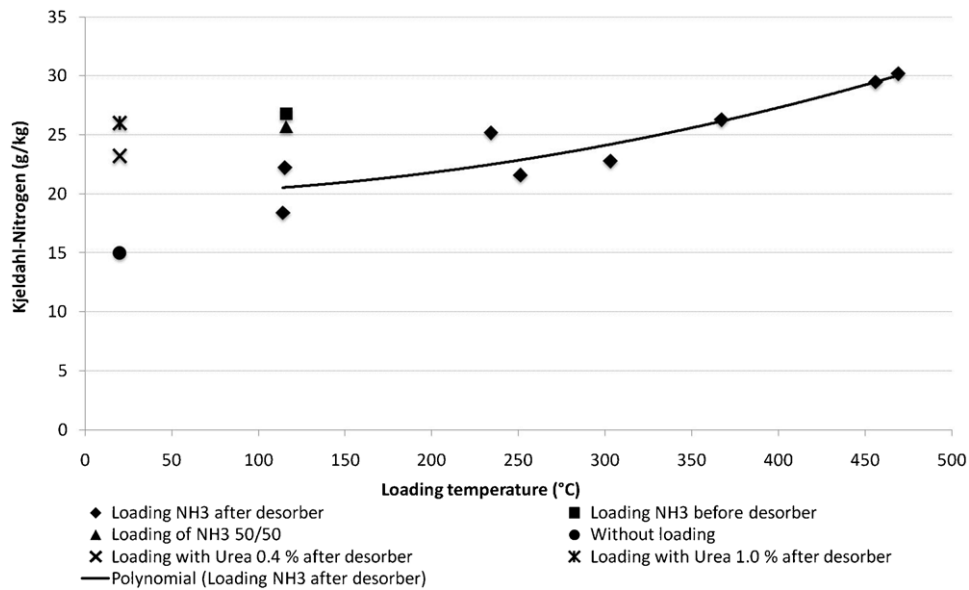
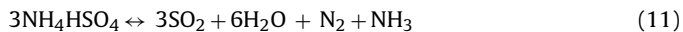


Fig. 4. Kjeldahl-Nitrogen results for the loading tests with ammonia on the three different types of activated coke.

During the regeneration process of the activated coke adsorbed with SO_2 , a decomposition of ammonium salts (ammonium bisulfate for the case study) occurs, as expressed in Eqs. (10) and (11) [9],



This way, there is an amount of ammonia available to react with the adsorbent causing a formation of reducing material that contains nitrogen, as shown in Eq. (12) [9].



This can also influence the Kjeldahl-Nitrogen content of the blank sample which is activated coke after desorber (AD). It is relevant to mention that this test alone cannot determine the type of nitrogen species added.

Fig. 4 shows that the increase in temperature has a positive effect on the mass load. It confirms that the highest achieved loading was

that done at the highest tested temperature (469°C). The trend line drawn by these results has no minimum at any temperature, opposite to the one calculated with the breakthrough time. This suggests that a shorter breakthrough time did not result in a lower addition of nitrogen into the activated coke.

A comparison of both lines is given in Fig. 5. In order to make the results comparable, an initial correction of the results for Kjeldahl-Nitrogen content was done, using the value for the sample without loading as the starting point. The measured value for the unloaded sample was subtracted from the values registered for the pre-loaded samples. This way it was possible to take into account the Kjeldahl-Nitrogen introduced exclusively as a result of the loading and not previously contained on the activated coke. Nonetheless, the conditions under which these two results were stated are different. The lower line shows the ammonia percentage mass load calculated with the breakthrough times, as said before. The upper line shows the corrected results of the Kjeldahl-Nitrogen contents on samples that were exposed to the ammonia

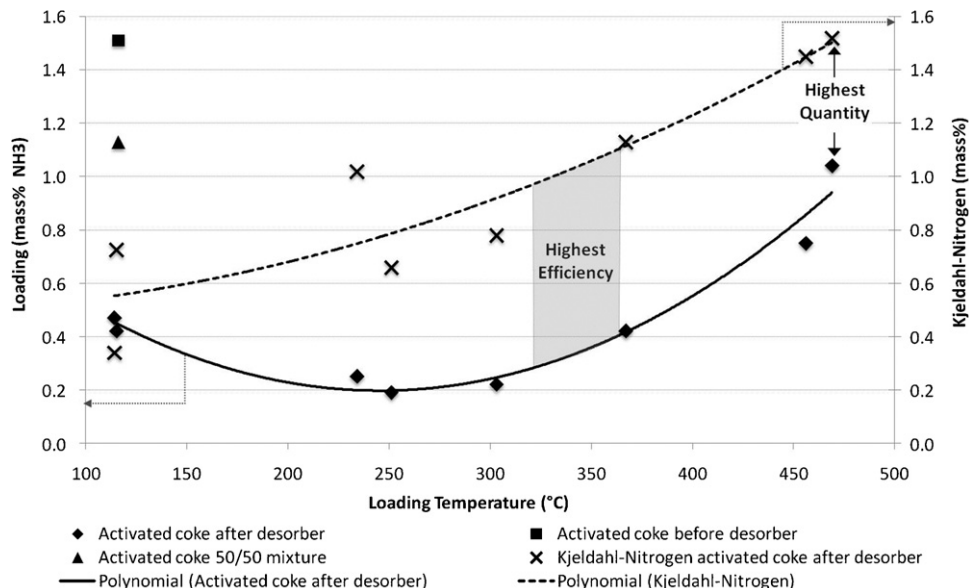


Fig. 5. Ammonia loading at breakthrough time and its related Kjeldahl-Nitrogen.

Table 4
Denitrification tests information.

Test code	Type of AC used	Loading conditions	
		Substance	Temperature (°C)
D-AD-NH3-115	After desorber	Ammonia	115
D-AD-NH3-469	After desorber	Ammonia	469
D-AD-Urea0.4	After desorber	Urea, 0.4 equiv. mass% of NH ₃	Room
D-AD-Urea1	After desorber	Urea, 1 equiv. mass% of NH ₃	Room
D-AD-00	After desorber	No loading	–
D-BD-NH3-116	Before desorber	Ammonia	116
D-ABD-NH3-116	50/50	Ammonia	116

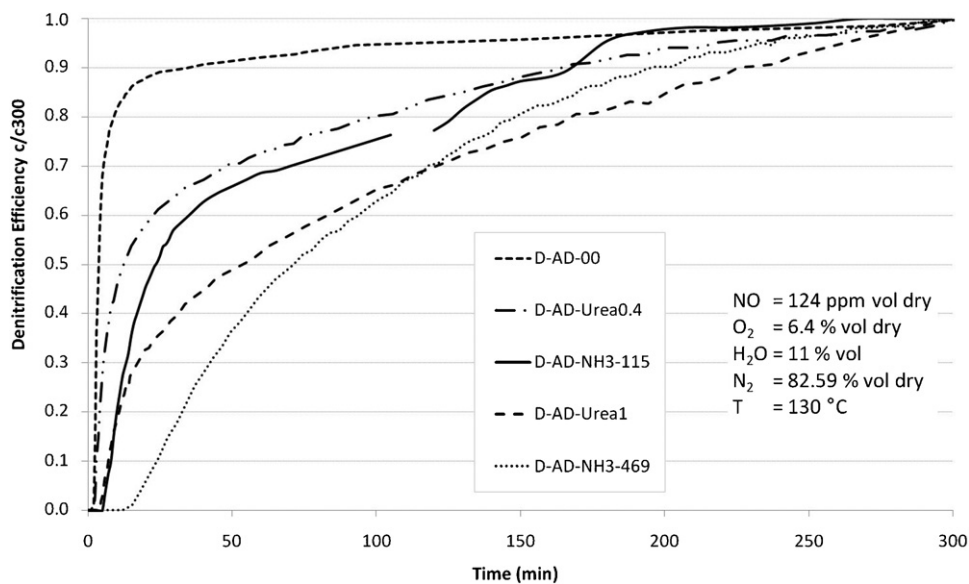


Fig. 6. Denitrification test efficiency with c/c_{300} : effect of loading temperature and loading substance.

not only at the breakthrough time but also 10 min after it, in every case.

The comparison of both lines shows that the position of highest loading quantity is located in both cases at the highest tested temperatures. Additionally, by the comparison of these two lines a region of highest efficiency is determined in which the ratio of ammonia uptake to ammonia loaded is

lowest. This region is located approximately between 320 and 370 °C.

6.2. Urea loading results

After loading with urea (ammonia equivalent of 0.4 and 1 mass%), the samples were also tested for Kjeldahl-Nitrogen con-

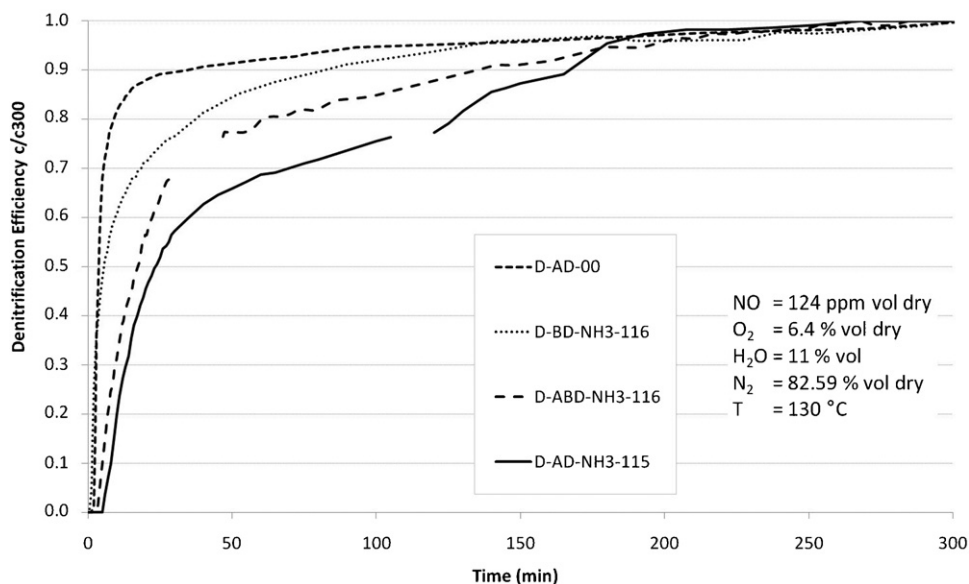


Fig. 7. Denitrification test efficiency with c/c_{300} : effect of sulfur components content.

tent (Fig. 4). The quantities found in these samples can be compared to the values for ammonia loading at temperatures between 300 and 370 °C. In the case of these investigations, the urea loading was done at room temperature.

6.3. Results of the denitrification tests

The results for the previously discussed loading tests enabled identification of the highest levels and efficiencies of loading. However, these tests alone will not enable to determine the effectiveness in their application. In order to evaluate this, denitrification tests with the pre-loaded activated cokes were done. In total, seven denitrification tests were guided and are listed in Table 4. The results obtained after the determination of the denitrification efficiency with the analysis c/c_{300} are shown in Figs. 6 and 7.

In these graphs the calculated c/c_{300} efficiencies for 7 samples are shown. Two discontinuities are present in these graphs. On the one hand, a gap on the line for the test D-AD-NH3-115, representing an opening of the bypass available in the testing plant. On the other hand, a discontinuity on the line showing the efficiency of test D-ABD-NH3-116 (Fig. 7), caused by an involuntary oxygen failure in the system.

The test D-AD-NH3-115 represents the current operating condition of the plant: loading of ammonia around the 114 °C and denitrification at 130 °C, using activated coke after desorber. The comparison of the results should then be done with respect to this line.

Taking into account that the efficiency in Figs. 6 and 7 increases downwards and that the test D-AD-NH3-115 line represents the current working conditions of the flue gas cleaning system, then two of the results can be considered to be more efficient: D-AD-NH3-469 and D-AD-Urea1. Test D-AD-NH3-469 for instance had the longest zero NO exit concentration. For the first 12 min the exiting concentration was registered as zero for this test, while all of the other tests had this condition for less than 6 min. Then the efficiency of D-AD-NH3-469 progressively decreased, but slower than all of the other tests. After 120 min, it crosses the D-AD-Urea1 curve.

The D-AD-Urea1 test shows the second best result of the group for the first 120 min. After this time this pre-loaded activated coke had the best efficiency in comparison with all the others and was the last to reach the $c/c_{300} = 0.97$ level.

The results of the denitrification test with urea equivalent 0.4 mass% of ammonia (D-AD-Urea0.4) were similar to the current situation (test D-AD-NH3-115). Although the efficiency was considerably lower, the performance was analog.

The comparison of the performance for the denitrification test of the three types of activated cokes (high, medium and low sulfur component contents) at temperatures around 114–116 °C, see Fig. 7, shows that the best results are obtained with the activated coke after desorber (low sulfur content). Even though the loading test suggested that the activated coke before desorber (L-BD-NH3-116) was able to trap a higher amount of ammonia than those after desorber, the denitrification test indicates that this ammonia was not available for NO reduction. This supports the initial assumption that a higher loading was achieved by the reaction of the ammonia with substances contained on the activated coke to form ammonium salts like ammonium bisulfate (NH_4HSO_4) referred in Eq. (8) and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) in Eq. (9), already discussed in Section 6.1. The ammonia contained in the reacted substances is no longer available for the reduction of NO. This can also be related to the fact that decomposition of the ammonium sulfate happens at temperatures above 250 °C [18].

Finally, regarding the denitrification test D-AD-00, sample without loading, the results indicate that, in any case, the ammonia loading enhances the NO reduction on activated coke. The activated coke alone can reduce the NO into nitrogen [14,19,20]. Neverthe-

less, the test D-AD-00 reached a c/c_{300} ratio of 0.9 in the first 30 min, which suggests that even with this additional mechanism existing, the reduction of the concentration of NO in the flue gas is considerably more efficient with the pre-loading of the activated coke.

7. Conclusions

The ammonia adsorption on activated coke is affected by temperature. For temperatures below 250 °C the adsorption decreases with the temperature, under the conditions investigated. For temperatures above this value the relation is directly proportional and the adsorption is enhanced by temperature. This indicates that below 250 °C a physisorption dominated process takes place, while above this reference the chemisorption, energy enhanced process, is dominant.

Higher amounts of ammonia are trapped by the activated coke samples containing higher amounts of adsorbed pollutants. Nevertheless, this ammonia is not available for the reaction with nitric oxide and therefore represents no improvement in the ammonia injection. This result could be possibly evaluated for activated cokes used for trapping ammonia, as a way to purify a gas stream.

The regenerated activated coke (low content of pollutants) is capable of adsorbing the highest amounts of ammonia when the process is done at 469 °C. According to the results, the ammonia loading in the system can be optimized by increasing the loading temperature above 350 °C.

It would be very interesting to get information on the performance for denitrification of the activated cokes which were loaded at intermediate temperatures (higher than 114 °C but lower than 469 °C), in order to make further analysis.

The reduction of nitric oxides by the tested activated coke is, in every case, improved with the pre-loading with ammonia or urea. The results showed that the performance of the activated coke loaded at 469 °C with ammonia, or that loaded with urea at 1 mass% ammonia equivalent, is more efficient than the one at the current conditions (ammonia loading at about 114 °C).

For the above mentioned reasons the current injection and the further denitrification process at the flue gas cleaning plant at Infraserb Hoechst can be improved by the use of activated cokes loaded either with ammonia at high temperatures or with urea.

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