Ammonia desorption from fly ash

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Abstract. The main source of ammonia in ash are residues from an unreacted NH_3 from the denitrification process, either from SCR or SNCR systems. The paper discusses the standards of NH_3 content in fly ash and presents the most commonly used methods of removing excess ammonia from fly ash. In the next part of the work the results of laboratory tests on NH_3 desorption are presented. Desorption was performed on samples of fly ash taken from the electrostatic precipitator of real PC boiler. Removal of NH_3 from the ash was carried out in a heating chamber at 130^0C and 150^0C and detected by an analyser equipped with a NDIR sensor. Additionally, at the temperature of 130^0C, the NDIR and analytical methods were compared (in accordance with the BN-750541-05 procedure) and the measurement uncertainty of both methods was estimated.

1 Introduction

The utilization of fly ash for construction purposes, i.e. for the production of concrete, requires that the ash meet certain criteria for physical and chemical properties. The fly ash obtained from boilers equipped with a flue gas denitrification system contains a certain amount of ammonium compounds due to the so-called "slip" of ammonia. Ammonia binds directly to ash as an unreacted substrate of denitrification reactions. In the case of SCR and SNCR installations with significant NH_3/NO molar excess, this leads to a substantial slip of NH_3 to the exhaust gas and ash. Due to used method the sources of ammonia are [1, 2]:

- SCR (selective catalytic reduction) - usually NH_3 aqueous solution,

- SNCR (Select non-catalytic reduction) - usually a 40% solution of $CO(NH_2)$ urea.

In an alkaline environment (concrete, mortar, etc.), ammonia is released to the atmosphere in molecular form. The presence of ammonium compounds in concrete does not

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unfavorably affect on its properties, however, it is an undoubted trade disadvantage, especially when the concrete is used in closed rooms. Currently there are no official standards for the content of ammonia in fly ash in Poland. Depending on the specification of the test site (including ventilation, air conditioning), it was found that the smell of ammonia is not perceptible in the case of fly ash containing not more than 100 to 200 mg NH_3/kg. It was assumed that the maximum ammonia content in ash should not exceed 100 mg NH_3/kg (U.S.A.), also lower values appear, up to 50 mg NH_3/kg (Germany). Meanwhile, the ash from the SCR plant can contain up to 2 500 mg NH_3/kg, which makes it unsuitable for use in the construction industry. Removing ammonia from fly ash would therefore be beneficial from the point of view of both the producer and the recipient.

The amount of ammonia and ammonium salts present in the fly ash is related to the amount of ammonia in the exhaust gas. According to the literature, up to 80% of ammonia from SCR is absorbed on fly ash [3]. Mostly, ammonia in fly ash occurs in the form of ammonium salts (mainly ammonium sulphate and ammonium bisulfate). There are also smaller amounts of other salts, such as ammonium chloride. In addition to the formation of ammonium salts, ammonia can also be adsorbed on the surface of ash particles, especially if the ash contains some unburned carbon. The reaction of carbon with ammonia takes place at a temperature of 200-400°C and leads to the binding of a functional group on the surface of coal [3]. The studies presented in [4] show that a sample of coal-containing ash is characterised by a greater adsorption of ammonia than a sample without carbon. In addition, it can be noticed that the carbon in ash shows a decrease in ammonia adsorption in increasing temperature, i.e. at a lower temperature, more ammonia passes to ash, less to gas phase [4].

2 Methods of ammonia desorption from fly ash

2.1 Thermal methods

Thermal methods of removing ammonia from ash are characterized by lower investment costs than chemical methods. Typically, these methods are based on desorption of ammonia at 300-450°C [5].

2.1.1 ERC Method (Energy Research Center)

In this method the ash from silo is placed into the fluidized bed reactor using air as fluidizing medium. During the process, the heated air flow continuously through the ash bed. Possible ash agglomerates are broken down by the acoustic method, through the waves generated by the acoustics generators. The method is used for ash with 500-1000 ppm concentration of ammonia. The release of ammonia starts at 150°C and the constant process temperature is 343-398°C. The process allows removing up to 90% of ammonia. This technology is not currently used industrially and remains in the testing phase. An unquestionable disadvantage is the necessity of using sound systems to break up the ash agglomerates in the reactor. The ERC method tests concern ash with an ammonia content above 500 ppm, and there is no data on its efficiency for lower concentrations [6].

2.1.2 Carbon Burnout

In this method ash is fed into fluidized bed reactor were unburnt carbon in ash is burnout. The process takes place in a reactor at a temperature of about 700°C with a residence time of ashes in the reactor for 45 minutes. During combustion in high temperature ammonia

compounds are decomposed. The process allows to obtain ash with an ammonia content below 5 ppm. In addition, the coal contained in the ash is burned (reduction of TOC), which improves its properties in terms of the use in construction. This method is used on a large scale in the U.S.A. [7].

2.2 Chemical Methods

2.2.1 STI Method

In solutions of ammonium salts with pH above 7, the ammonia is released into the gas phase. This is the basis of most chemical methods for removing ammonia from fly ash. Water injection to the ash causes the increase of its pH and thus the release of ammonia to the gas phase due to the neutralization of acidic residues which are formed with ammonia. This reaction takes place in the process of producing cement from ash [8].
In the STI method small amount of water with alkaline compounds is injected to the ash. Ammonia released from the ash is then catalytically reduced or removed in wet absorbers. In the STI process it is possible to reduce the mass fraction of ammonia in ash to a value below 100 ppm, which is the accepted limit of detection in construction products. The technology involves the use of water, which in itself causes the release of some of the ammonia to the gas phase, but the addition of alkaline compounds increases the efficiency of the process. According to [9], the addition of water is about 5% (<20%) and alkaline compounds about 5% (<10%). Moreover solution of 0.25-1% CaO or $Ca(OH)_2$ is dosed. The process takes place at a temperature of 15-65.5°C for 15 to 30 minutes.

2.2.2 ASMTechnology

The ASMTechnology method assumes the use of $Ca(ClO)_2$ calcium hypochlorite as a strong oxidizing agent. The efficiency of this process is up to 95%. Ammonia contained in the ash is oxidized to molecular nitrogen, additionally chlorine ions are released. The degree of removal of ammonia depends on the pH of the ash, time and temperature of the reaction and the amount of reagent used. In practice, 1.0-1.5 times the molar excess of calcium hypochlorite to ammonia is used [10].

2.2.3 Ozonation

The laboratory tests conducted in [11] show the results of ammonia removal from ash by ozone oxidation. The ash may have catalytic properties in the oxidation of ammonia with ozone at ambient temperature (23 °C) [12]. In this process air with high humidity is supplied to the ash in the order to keep moisture of ash at level of 1-5%. To the semi-dry ash obtained in this way, ozone, a mixture of air with ozone or oxygen and ozone as an oxidizing agent is supplied. Table 1 shows the results of the experiment for the initial NH_3 content in ash of 1200 ppm. In each case, ozone caused a reduction of ammonia and the best result was obtained for a mixture of 2% ozone at 150 °C.

Table 1. Results of NH_3 removing using ozonation [11].

Oxidazing agent	NH_3 concentration in ash after process, ppm
O2 (150°C)	1200
O3 4000 ppm (20°C)	850
O3 4000 ppm (150°C)	500
O3 2% obj. (150°C)	400

2.2.4 Catalitic Methods

These methods are based on the reaction of selective catalytic oxidation of ammonia (SCO - selective catalytic oxidation) acc. reaction (1):

$$4\,NH_3 + 3\,O_2 \rightarrow 2\,N_2 + 6\,H_2O \qquad\qquad (1)$$
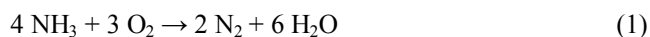
The different catalysts can be used in this process, for example: CuO, Fe_2O_3, Co_3O_4, MnO, V_2O_5, CuO/La_2O_3, CuO/RuO_2. The best efficiency obtained is 60% conversion of ammonia to N_2 with nitrogen selectivity over 90%. The process temperature is 300-450°C. The advantage of catalytic methods of ammonia removal is the ability to conduct the process in a stream of dusty exhaust gas, without the need to separate the ash. The disadvantage is the necessity of installing the catalyst and the possibility of its deactivation ("poisoning") by SO_2 or heavy metals contained in the exhaust gas. Studies carried out so far assume the utilization of water vapour resistant catalysts [12-13].

2.2.5 Wet Methods

Studies on the solubility of ammonium compounds show that after 10 minutes of aqueous extraction, about 85% of ammonia is released from ash into water. In this process ammonia is removed in fluidized reactor in contact with high humidity air or by rinsing of dusted exhausts in a reactor with strongly turbulent flow. This allows removing from the flue gas ash particles up to 0.5 μm as well as gaseous components soluble in water, including NH_3 [14-16].

3 Methodology

For experiments the fly ash was separated from the electrostatic precipitator of a coal-fired pulverized coal boiler. In the order to increase ammonia concentration in ash, the ash were extra enriched by gaseous ammonia. Because the initial content of ammonia in the ash was less than 50 $mgNH_3/kg$. The increase of ammonia content in ash sample were achieved using the NH_3 gas stream supplied from the bottle. This value was increased to 453 mg NH_3/kg. An ash sample of 200 g was placed in a flat crucible in a constant temperature zone in a closed heating chamber. The air flow through the chamber was set at 2 dm^3/min and controlled by the flow regulator according to Figure 1.
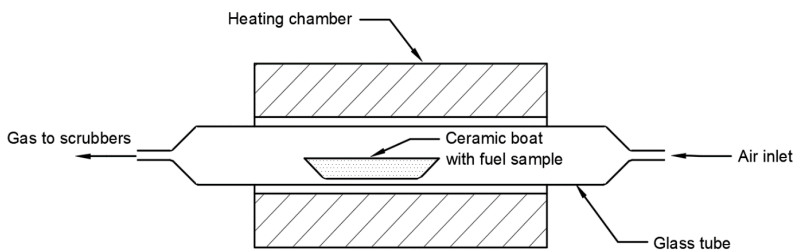
Fig 1. Scheme of the lab facility.

The test were conducted at two temperatures: 130⁰C and 150⁰C. NH_3 content in outlet of combustion chamber were measured by two methods:
- Using the SIEMENS U6 gas analyser, equipped with NDIR (Non Dispersive Infrared Sensor) NH_3 sensor. This gas analyser is dedicated for NH_3 measurements in two ranges 0 – 100 ppm vol. and 0 - 1000 ppm vol. The gas sample flowing through the analyser must be adequately dedusted (particles d_z <1μm) and dried. For this purpose, it is possible to use an exhaust gas conditioning system using a Peltier cell, which allows quick water condensation from the exhaust gas and its immediate removal. However, one should remember about the possibility of NH_3 being absorbed in the removed condensate, which may lower the real values of the measured NH_3.
- Using the standardized procedure BN-75 0541-05. This method can be used for determination of ammonia content in gaseous fuels and crude (raw) gases from combustion of carbon origin fuels. Is used in the determination of ammonia regardless of its content in the gas. The method is based on the quantitative absorption of ammonia in a solution of sulfuric acid. The excess sulfuric acid is back-titrated with the standard solution of sodium hydroxide. Apparatus, instruments and reagents used to measure:
    - Two gas scrubbers with a capacity of 200 cm3 each, including one with a filter
    - Laboratory gas meter
    - Sulfuric acid solution 0.01 N
    - Sodium hydroxide solution 0.01 N
    - Methyl red (alcoholic solution).

The scrubbers contain of 0.01 N sulfuric acid solution of 60 cm^3 and 1 cm^3 of methyl red alcohol solution. The apparatus has been set up so that the gas flow path to the scrubbers is as short as possible and all connections are sealed. After the gas was bubbled through the scrubbers, the solution from scrubbers 1 and 2 was quantitatively transferred to a flask and the excess of 0.01 N sulfuric acid solution was titrated with 0.01 N sodium hydroxide solution.

Ammonia content in the gas X is calculated as $gNH_3/100 \ m^3$ of gas according to:

$$X = \frac{0.01713 \ (a-b) \ 10^3}{V_o} = \frac{1703 \ (a-b)}{V_o} \qquad (2)$$

where:
a – volume of 0,01 N sulfuric acid solution, cm^3
b – volume of 0,01 N sodium hydroxide solution, cm^3
V_o – volume of gas, cm^3
0,01713 – amount of ammonia corresponding to 1 cm^3 0,01 N sulfuric acid solution.

3.1. Measurement uncertainty

An account of measurement uncertainties should be a part of every correctly performed experiment, especially when comparing different measurement methods of the same value in an indirect way. The determination of measurement uncertainty has a significant impact on the formulation of correct and reliable measurement conclusions [17]. In the power industry, the determination of measurement uncertainty may also be related to compliance with emission standards [18]. Expanded uncertainty is the most widely used method when it comes to industrial installations measurements. In the presented study, calculations of the expanded uncertainty with the extension coefficient k = 2 for the 95% confidence level were presented. The accuracy of the NH_3 measurement by the analytical method consists of all the solutions volumes measurements, the subjective assessment of the color change of the solution, as well as the measurement uncertainty of the gas sampling device. When using the Siemens Ultramat U6 analyzer, Table 2 presents the parameters influencing the measurement result, which are provided by the manufacturer [19].

Table 2. The influence of different parameters on the measurement results of the Siemens U6 gas analyzer.

Measurement quality	
The output sygnal change	<+/- 1% smallest possible measurement, range according to the nameplate with a specific damping constant for the analyzer (corresponding to +/- 0,33% with 2σ)
Zero drift	< +/- 1% measuremnt range / week
Range drift	< +/- 1% measuremnt range / week
Repeatability	Between 0,1% annd 1% depending on the model
Linearity deviation	<0,5% full scale value
Influencing variables	
Temperature	1% measurement range / 10 K (unheated version)
The pressure of the measuring gas	With pressure compensation <0,15% of the setpoint; with 1% change under pressure
The stream of the measuring gas	Not important
Power supply	<0,1% range of the output signal at the rated voltage +/- 10%
Ambient conditions	It depends on the type of gas uptake: If it contains a measured component or contains a component that affects cross-sensitivity

3 Experimental results

Table 3 shows the amount of NH_3 released from the ash after 10, 20, 30, 60 and 120 minutes of desorption at 130°C and 150°C. The amount of NH_3 (in mg NH_3) was calculated from the Siemens U6 analyzer measurement and presented and as a percentage of the initial NH_3 content in the ash sample. The concentration of NH_3 ppm vol. as a function of experiment time is shown (Figure 2). A visible effect of temperature on the release rate of

NH_3 from ash can be observed. The initial concentration of NH_3 at 130□C was 710 ppm vol. whereas at 150□C it was 858 ppm vol. Stabilization of desorption was obtained at 130□C after 3 hours and 12 minutes, while at 150°C the time was shorter - 2 hours and 37 min. Further maintenance of the samples in the heating chamber did not affect the NH_3 concentration in the outlet gas.

Table 3. Amount of NH_3 released from the ash after 10, 20, 30, 60 and 120 min of desorption measured using the U6 analyzer.

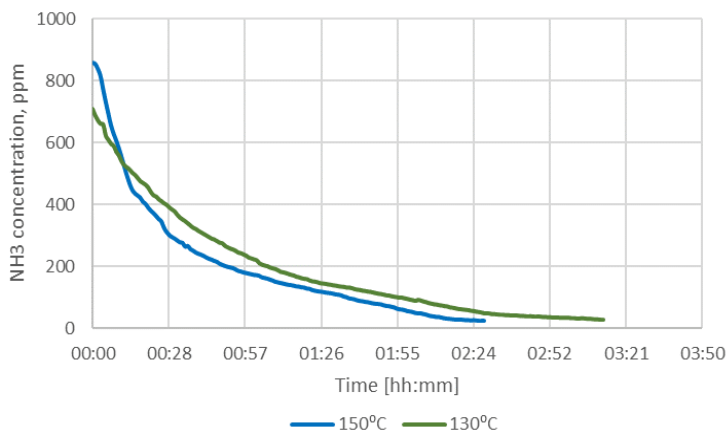| Reaction time, min	130°C		150°C	
	mg NH_3	% initial value	mg NH_3	% initial value
10	15	16	17	19
20	27	30	29	32
30	37	41	38	42
60	54	59	59	65
120	71	78	80	88

Fig 2. Concentration of NH_3 at the outlet of the heating chamber for the desorption process at 130°C and 150°C

For a more accurate analysis of the ammonia desorption process, the data presented in the Figure 3 was calculated. The rate of NH_3 concentration decrease ppm/min was calculated. This data shows that for the temperature of 150□C the maximum rate of 43ppm NH3/min was reached after about 3 minutes, whereas for the temperature 130□C it was 36ppm NH3/min after a time of about 4 minutes. At a higher temperature level (150 °C) the process takes place more rapidly. The significant drop in the concentration of NH_3/min (≥10 ppm / min) at 150°C takes place during the first 36 minutes of experiment, while for temp. 130 °C for 31 min.

In the further part of the study, the analytical method of NH_3 measurement (in accordance with the BN-75 procedure 0541-05) was compared with the U6 analyzer. The values were converted into an amount of NH_3 released into air and the percentage value of the initial NH3 content in the ash sample. In Figure 3 a comparison of the NH_3 amount released from ash after 10, 20, 30 and 60 minutes of desorption at 130°C is shown.
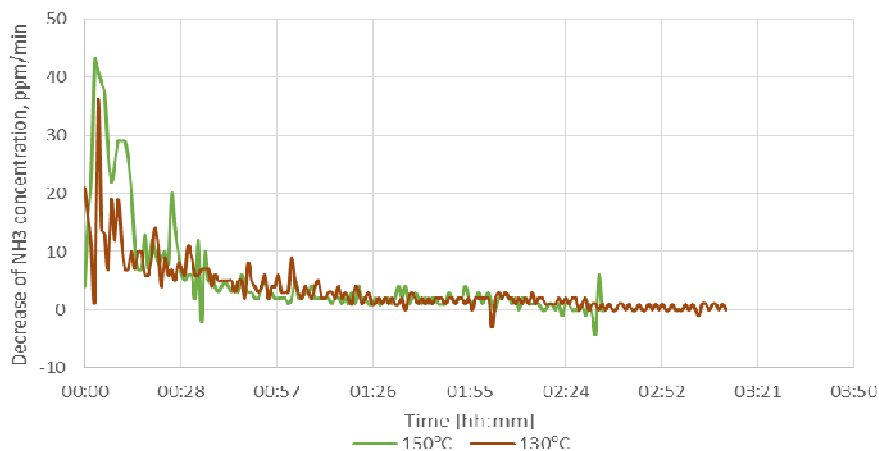
Fig 3. Decrease of NH$_3$ concentration during desorption process at 130 °C and 150 °C.

For a more detailed analysis, the uncertainty account was made using the extended uncertainty method with the extension coefficient k = 2 for the 95% confidence level. The uncertainty for the analytical method was +/- 18.9% of the released amount of NH$_3$, while for the U6 analyzer it was +/- 9.25%. It can concluded that the U6 analyzer measurement is almost twice as accurate as the method presented in the analytical method. However, this result is influenced by a small population of samples for both discussed methods. In all cases, the lower values obtained by the analytical method indicate that the absorption of NH$_3$ in the condensed water (moisture from air and ash) removed in the exhaust conditioner had a little effect on the result of the U6 analyzer. Only in the lowest measured range after 10 minutes, similar values were obtained for 130 °C (14 and 15 mgNH$_3$) within the limits of measurement uncertainty. In the remaining time ranges, the values of the released NH$_3$ do not differ significantly.
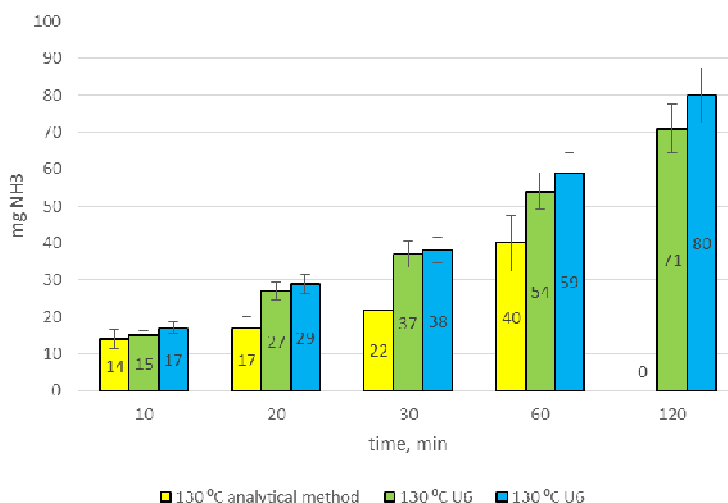

Fig 4. Amount of NH$_3$ released from ash at 130°C for two measuring methods (U6 and analytical metric) and at 150°C (U6 analyzer) with measured uncertainties.

4   Conclusions

Desorption of ammonia from fly ash is an important process that can be applied in industry. It is mainly related to meeting the fly ash quality standard required by customers from the civil engineering industry. In presented research NH_3 desorption was carried out from fly ash taken from the electrostatic precipitator from coal fired power plant. The experimental part of the research presents the results of ammonia desorption form ash placed in the heating chamber. The desorption was carried out at two temperature levels: 130 ⁰C and 150 ⁰C. For the 130 ⁰C two measuring methods were compared: the analytical method (according to polish standard BN-75 0541-05) and the Siemens U6 gas analyzer with NDIR sensor. The uncertainty analysis shows nearly 2 times greater accuracy of measurements using an NDIR analyzer comparing to the analytical method. The ammonia desorption from the ash is a rapid process in the first phase (30 minutes). The release of gaseous NH_3 can be dangerous for people working with the power installation, as well as people who collect and transport the ash. The measurements made with the U6 analyzer indicate that for the first 30 minutes 41-42% of the initial value of NH_3 contained in the ash is released, after 60 min it is 59 - 65%, and after 120 minutes it is 78 - 88%, depending on the process temperature (130 ⁰C – 150 ⁰C). Stabilization of the NH_3 concentration was observed after 3 hours and 12 minutes for a temperature of 130 ⁰C, while for a temperature of 150 ⁰C it was 2 hours and 37 minutes. Further research should take into account the influence of other ash compounds, its elemental composition and the size of the particles on the NH_3 desorption process. The SEM-EDS analysis of the tested samples would be a purposeful addition.

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