Magdalena Mazur

Tomasz Janda

    Electricity de France, Cracow Division, Poland

Witold Żukowski (witold.zukowski@pk.edu.pl)

    Faculty of Chemical Engineering and Technology, Cracow University of Technology

CHEMICAL AND THERMAL METHODS FOR REMOVING AMMONIA FROM FLY ASHES

CHEMICZNE I TERMICZNE METODY USUWANIA AMONIAKU Z POPIOŁÓW LOTNYCH

Abstract

The presence of ammonia in ashes (i.e. ammonia slip) is a direct consequence of the methods used for denitrification – selective catalytic and non-catalytic reduction (SCR, SNCR). The excess unreacted ammonia used in both of these methods passes as a constituent to ash, impairing its properties, and thus affects the quality of the commercial product. The summary of the available methods for removing NH_3 from fly ashes is presented. Both chemical and thermal methods of removing NH_3 are described. The results of the chemical methods depend on the kind of additional reagents used and composition of fly ashes. Thermal methods seem to be simpler and easier to use, but they are used mainly on the smaller scale.

Keywords: flyash, deammonisation

Streszczenie

Obecność amoniaku w popiele (tzw. poślizg amoniaku) jest bezpośrednią konsekwencją stosowanych metod odazotowania spalin – katalitycznej i niekatalitycznej selektywnej redukcji (SCR, SNCR). Stosowany w obu tych metodach nadmiar amoniaku przechodzi w formie nieprzereagowanej do popiołu, pogarszając jego właściwości użytkowe i tym samym wpływając na jego jakość jako produktu komercyjnego. Prezentujemy przegląd dostępnych metod usuwania NH_3 z popiołu, chemicznych a także termicznych.Efektywność metod chemicznych zależy od rodzaju zastosowanego substratu i składu popiołu lotnego. Metody termiczne wydają się prostsze i łatwiejsze w zastosowaniu, ale są używane głównie w instalacjach o mniejszej skali.

Słowa kluczowe: popiół lotny, deamonizacja

1. Introduction

The adaptation of energy production facilities to meet the new and more demanding standards for emissions of nitrogen oxides (NOx), which came into effect on 1 January 2016, involves many aspects. A direct consequence of the methods of denitrification –both catalytic and non-catalytic selective reduction (SCR, SNCR) is the presence of ammonia in ashes (i.e. ammonia slip). Both methods create excess of unreacted ammonia, passing to the flue gases, bonded to particles of fly ash in the free form or as a part of ammonia salts, and degrading its properties, and thereby affecting the quality of commercial solid products [1–4].

Ammonia is widely used in industrial processes, in large quantities. It is a combustible gas, toxic, corrosive, and irritantto the human mucous membranes. These properties mean that ammonia is fraught with danger for human health and life. When bound with fly ash it may be released as a result of the operation during storage or during processing of materials, which in its composition contain fly ash[4].

The report made by the Electric Power Research Institute (EPRI) shows that the problems related to the ammonia content in fly ash have become a problem for coal plants in recent years, due to the increased use of ammonia in the process of the denitrification of flue gases. The study was conducted on the basis of samples from Conectiv's BL England station, Georgia Power's Plant Yates and the Orlando Utilities Commission (Table 1) [5].

Table 1. Examples of fly ashesand its ammonia concentration [5]

Sample name	Source unit	Unit type	Coal type	Ammonia source	Nominal ammonia concentration
Yates	Georgia Power, Plant Yates, Unit #5	CE, T-fired	Eastern Bituminous, High-VolatileA, 1.2% Sulfur	FlueGas Conditioning	150 ppmw
Stanton	Orlando Utilities Commission, Stanton, Unit #2	B&W, Wall-fired	Eastern Bituminous, High-Volatile A, 1.1% Sulfur	SCR	100 ppmw
BL England	Conectiv, BL England, Units #1 and #2	B&W, Cyclone-fired	Eastern Bituminous, 2 % Sulfur	SNCR	700 ppmw

Based on the study on the release of ammonia from the ash, it has been shown that for objects that will be dealing with sales of ammonia containing ash, the chemical composition of the ash can be significant. From this point of view, there is the possibility of the release of ammonia during the subsequent use of fly ash as an additive to, for example, concrete. It seems that particular ash processing will force secretion of ammonia regardless of the ash characteristics. Therefore the total amount of ammonia present dictates the height of the release of ammonia, and whether it will be released or not [5].

While an analysis of the ammonia injection to electrostatic precipitators has shown that this may result in an increase in the ammonia content in the ash up to 2000–2500 ppm, resulting in ash

that is not suitable as a concrete additive. Moreover, it was shown that ammonia slip at the level of 2 ppm may result in increased ammonia content in the fly ash above 100ppm and thus prevents the sale of such a non-market ash [6]. Fly ash as a cement additive must meet appropriate criteria in terms of physical and chemical properties. A higher ammonia content leads to more intense and unpleasant odour generated during processing. Despite the fulfilment of the basic parameters of ash, an unpleasant smell is not acceptable, thus based on industrial practice it was concluded that the ashes should contain up to 100 ppm of ammonia. On the other hand, power generation plants can generate fly ash ammonia contents of 200 to 2500 ppm [7].

In such cases it is necessary to modernize the ash processing plant to implement the chosen method of removing excess ammonia, occurring mainly in the form of ammonium sulphate [6]. It should be mentioned that no Polish and EU regulations on permissible level of NH_3 in fly ash have been developedthus far. Such regulations have been developed in particular countries due to the possibility of further utilization of fly ash.

2. The origin of NH_3 in by-products of combustion – mechanism of ammonia transfer to ash

Ammonia is a polar, colourless, toxic, irritating the mucous membranes, gaseous compound with a characteristic odour. It condenses into a colourless liquid at a boiling point of –34°C (239.74 K), with a high heat of vaporization (1.3 g/kJ). It is most often used in refrigeration. It is soluble in water, where it is present in the form of ammonium ion (reaction 1), due to its interaction with water molecules and generation of hydrogen bonds.

$$NH_{3(g)} + H_2O \leftrightarrow NH_4^+ + OH^- \tag{1}$$

Due to its high solubility (1 volume of water dissolves 1176 volumes of $NH_{3(g)}$ at. 0°C) in aqueous solutions it occurs in the undissociated form, and to a certain degree it dissociates (in a solution of conc. 0.1 mol/dm³ only 1% ammonia molecules are present in the form of ions NH_4^+). Consequently, aqueous ammonia solutions behave like a weak base. Solubility decreases with increasing temperature and increases with the increase of $NH_{3(g)}$ partial pressure (equation 2 and 3) [8, 9].

$$k_H = \frac{NH_{3(aq)}}{p_{NH3(g)}} \tag{2}$$

$$nk_H = \frac{4092}{T - 9.70} \tag{3}$$

wherein:

k_H – Henry's constant;
$NH_{3(aq)}$ – the concentration of ammonia in aqueous solution;
$p_{NH3\,(aq)}$ – partial pressure of ammonia.

Ammonia in aqueous solution is present in two chemical forms which differ significantly in their toxicity: unionized, toxic NH_3 and ammonium NH_4^+ (with low toxicity). A state of equilibrium between the two forms is represented by the equation (4) [8, 9].

$$NH_3 \cdot nH_2O_{(aq)} \leftrightarrow NH_4^+ + OH^- + (n\text{-}1)H_2O_{(l)} \tag{4}$$
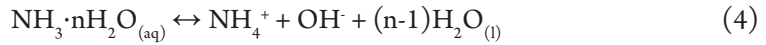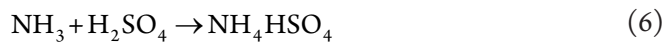
The ratio of both forms of ammonia is mainly dependent on the pH of the solution and, to a lesser extent, on temperature. The increase in the pH causes shift of the equilibrium to unionized form of NH_3. At pH = 9.2 there is a balance between the concentration of both forms. As temperature rises, the equilibrium moving towards lower pH values [9].

Ammonia bonds to ash directly as unreacted substrate used in flue gas denitrification systems. Depending on the method used for denitrification, its sources are [8, 9]:
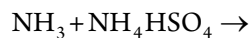
- ▸ SCR (selective catalytic reduction) Installation – due to addition of 24% solution of NH_3, in stoichiometric excess: 1.02–1.1 with respect to NO_x.
- ▸ SNCR (selective non-catalytic reduction) Installation – addition of 40% urea solution $CO(NH_2)_2$, in stoichiometric excess: 2.0–3.1.

Excess of ammonia reacts with other gaseous components of flue gas to form ammonium salts (sulphates, carbonates, chlorides), which can be in solid or liquid form, depending on the temperature. The latter can eventually evaporate and leads to the formation of solids. This process is promoted by a steam and increased temperature. In the largest amount (approx. 75%) ammonium hydrogen sulphates and sulphites are formed (Equation 5–7). Sulphites have a strong hygroscopic character and are therefore trapped in electrostatic precipitators – no significance for the process [9]. The SO_3 presence in the exhaust gas is the main factor leading to the formation of sulphate and bisulphates [9, 10].

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4 \tag{5}$$

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4 \tag{6}$$

$$NH$$

$$\tag{7}$$

$$NH_3 + NH_4HSO_4 \rightarrow$$

To simplify the process of passing ammonia to ashes, two steps are proposed [8, 9]:

a) Intrinsic ammonia adsorption: NH_3 occurs as molecules adsorbed on the surface of the ash particle creating chemical bonds, an important role in the mechanism of the process is played by active acid sites on the surface of the ashes particles; the process is reversible;

b) Ammonia deposition: NH_3 is present as an ammonium salt (mainly sulphates and bisulphates), which adhere to the grain ash.

Ammonium bisulphate, is a solid compound with the chemical formula $(NH_4)HSO_4$, a decomposition temperature of 147°C and a very high solubility in water (for the pure $(NH_4)HSO_4$ has a solubility of 1000 g/dm³). It is soluble in some organic solvents (e.g. methanol) and insoluble in acetone. It is a product of incomplete neutralization of sulphuric acid (VI) with ammonia, or may result from thermal decomposition of ammonium sulphate (reaction 8):

$$(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3 \qquad (8)$$
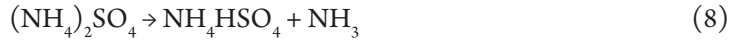
It has a strong hygroscopic character, a high viscosity (in liquid form) and therefore also causes corrosion and slag formation. In contrast, secondary component–ammonium sulphate is a dry, non-sticky powder having a particle diameter of ≤10 µm and unlikely to undergo deposition, but is carried along with the flue gas to electrostatic precipitators, where is not trapped and is considered to participate in PM10 emissions [9, 10].

In a solution of ammonia salts, when pH increases above 7 it can cause the transition of ammonia into the gas phase. It is precisely this phenomenon which is the most significant in the context of ammonia release from the ashes. For example, if the ash is wet, basic compounds can react with water, pH may be high and NH_3 is released in gaseous form. This phenomenon occurs because of the neutralization of acidic groups of solids, which previously bonded the NH_3. This reaction is often seen in the processing of ash in cement production plants [10].

The literature [5, 11–15] indicates a close relation between ammonia adsorption and qualitative composition of the ash and the conditions of its formation. With increasing amounts of unburnt carbon, the possibility of NH_3 adsorption increases –ashes with a higher content of silicates and aluminosilicates have a lower affinity for ammonia. It was confirmed that the oxides present on the surface of the carbon adsorb ammonia. This is explained by the fact that the acidic functional groups are combined with oxides and act as a Bronsted acid with respect to ammonia as a base. As a result of acid-base interaction proton transfer can occur to produce an ammonium ion NH_4^+, which then interacts with an acidic or amide side causing formation of imides [11]. In other words, the existence of the ash surface acidic groups facilitates attachment of ammonia –by creating a kind of "active site" which attracts NH_3 molecules. The increase of the acid groups is observed mainly for ash from lower quality coal. Conditions conducive to the adsorption of ammonia are a reducing atmosphere and a rapid lowering of temperature, causing a glassier phase in the ashes [11].

3. Chemical methods of removing ammonia from fly ash

3.1. STI Technology

STI a patented technology which involves the addition of a small amount of water and alkali to the ashes in order to release ammonia, and then its catalytic reduction, or uptake during processing in wet absorbers. The process reduces the total ammonia concentration to less than 100 ppm by weight of the dry fly ash. This value eliminatesa detectable ammonia

odour in the product during use, and thereby does not impair other properties of the product. Key features of the STI process are [6, 7, 16]:

> ▸ The addition of water: thisis efficient alone, but more efficient when combined with other methods.
> ▸ The addition of alkalis: accelerates the reaction the release of NH_3, but too much addition causes the ashes to be useless.

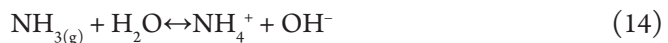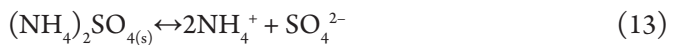The main parameters, which were given and claimed in the patent granted:

> ▸ addition of 5% H_2O (< 20%),
> ▸ addition of 5% alkali (< 10%),
> ▸ addition of 0.25–1% CaO, $Ca(OH)_2$
> ▸ process temperature 15–65.5°C
> ▸ process time 15 min (below 30min).

The principle of the method is displacement of a weaker base (NH_4^+) in the salt ($(NH_4)_2SO_4$) by a stronger ion (Ca^{2+}) according to Reaction 9. The chemical reaction takes place in a thin surface film of the aqueous phase surrounding the ash particles which is formed as a result of the addition of water while vigorous stirring. A larger contact area and the process of diffusion in the liquid phase accelerate the reaction rate. Steps which can limit the speed of the process are: the hydration reaction of quicklime (reaction 10), the migration of calcium ions and hydroxyl to the solution, dissociation of $Ca(OH)_2$ which increases the pH of the mixture (reaction 11), which are accompanied by precipitation of the solid (reaction 12). Ammonium salt existing in the mixture is soluble in water, goes into the ionic form (reaction 13). Followed by reaction with hydroxyl ions goes into gaseous ammonia (reaction 14) [6, 7, 16].

The overall reaction is as follows:

$$(NH_4)_2SO_{4(s)} + CaO_{(s)} \rightarrow 2NH_{3(g)} + CaSO_{4(s)} + H_2O_{(g)} \qquad (9)$$

Detailed reactions:

$$CaO_{(s)} + H_2O \rightarrow Ca(OH)_{2(s)} \qquad (10)$$

$$Ca(OH)_{2(s)} \leftrightarrow Ca^{2+} + 2OH^- \qquad (11)$$

$$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_{4(s)} \qquad (12)$$

$$(NH_4)_2SO_{4(s)} \leftrightarrow 2NH_4^+ + SO_4^{2-} \qquad (13)$$

$$NH_{3(g)} + H_2O \leftrightarrow NH_4^+ + OH^- \qquad (14)$$

The reaction of ammonium salts with lime is highly privileged because of a chemical imbalance. A key feature of the STI is the limited quantity of water (1 to 4%, typically 2 wt.%) and small amounts of alkali (< 2%). A larger amount of water is detrimental to the process – it causes dilution of the reaction system, and thus slows down the release of ammonia, at the same time it increases the moisture content of the ash, which must be subsequently removed from the

solid product. The pH of the resulting mixture of ash-lime-water should be higher than 10. Small amounts of alkali are added to provide this pH value, depending on the natural acidity of the ash. Therefore, this method is most suitable when the pH of the ash is high, the displacement of the equilibrium of the reaction is the easiest and requires minimal costs of raw materials[6, 7, 16]].

In subsequent publications, authors show the maximum efficiency of ammonia removal in the reaction of quicklime in the presence of 1–4% water at pH > 10 [9–11].Table 2 shows the dependence of efficient response time with respect to the amounts of substrates used under an unacceptable concentration of NH_3 to 100 ppm [6, 7, 16].

The usage of an equivalent amount of $Ca(OH)_2$ instead of CaO improves response time by eliminating the limiting step (Reaction 10), but on the other hand the reaction (10) is strongly exothermic and produces heat affecting the rate of the reaction and the phase transitions of water in the gaseous state. The usage of an equivalent amount of NaOH against $Ca(OH)_2$ decreases the efficiency of the reaction because of the extremely high values of pH > 14 and leads to ashagglomeration [6, 7, 16].

Use of an equivalent amount of $Ca(OH)_2$ instead of CaO improves response time by eliminating the limiting step (Reaction 10), but on the other hand the reaction (10) is strongly exothermic and provides heat affecting the rate of the reaction and the phase transitions of water in the gaseous state. Use of equivalent amount of NaOH relative to $Ca(OH)_2$ decreases the efficiency of the reaction because of the extremely high values of pH > 14 and ashagglomeration [6, 7, 16].

Table 2. Dependence of the reaction time on the content of the substrates, pH = 8.8 [7]

Alkali content	Water content	Reaction time [min]
0.25% CaO	4%	>> 15
0.5% CaO	4%	10
0.5% CaO	2%	> 15
1% CaO	2%	8
1% CaO	1%	>> 15
0.36% NaOH	4%	> 15
0.33% Ca(OH)$_2$	4%	> 15
0.66% Ca(OH)$_2$	2%	8
0.66% Ca(OH)$_2$	4%	4

In the process mentioned above, there are two stages in which ash is mixed with lime and water. The successively deammonized ash is transported to the dryers where, at approx. 65°C, evaporation of water from the ash takes place. Then the gaseous ammonia can be converted to nitrogen, or captured in water absorbers [7].

There are disadvantages of STI technology:
► It is necessary to build an ammonia – ash separation plant.
► Additional costs arising from the use of alkalis;
► The decrease in production efficiency associated with the need to remove moisture from the ash;

- The by-product, in the case of non-catalytic methods will be NH_3. Then it is necessary to use e.g. acid scrubbers. This is an additional element that causes an increase in capital expenditures.

The advantages of the installation of STI[6,7,16]:

- The high efficiency of the process – the reduction of ammonia from 87% at the end of the ammonia content of 100 mg/kg;
- The byproduct of the process of enrichment of ash is molecular nitrogen (N_2), which is an inert gas and does not increase the negative impact on the environment, in the case of the use of catalytic methods;
- Possibility of use N_2 for other purposes (e.g. explosion and fire protection, reducing the microbial degradation of biomass stored in a silo);
- The process occurs at ambient temperatures, drying the ash need only raise the temperature to 65°C;
- The final product is a high quality ash, which can be used as an additive for concrete production;
- The process of removing ammonia can be installed as a separate system in existing plants;
- The process has been implemented industrially since 1997;
- The ability to use fly ash from fluidized-bed boilers and dust;
- No restrictions on the DeNOx method(work with both SCR and with SNCR).

In Florida, two installations have been built: in Tampa and in Jacksonville. Both systems include the patented process, which reduces the content of ammonia in fly ash levels greater than 2000 ppm to < 75 ppm. The first plant capacity is 350.000 t/y. The installation includes three separators. On the other hand, the installation in Jacksonville contains two separators and the process of ammonia removal is 300.000 t/y. By 2013, 12 such installations have been implemented, i.a.: North America, Europe and Canada [17].

3.2. ASMTechnology

This technology involves treating the fly ash with calcium hypochlorite, $Ca(ClO)_2$, as a strong oxidizing agent[18]. The ammonia contained in the ash is oxidized to nitrogen with 95%efficiency, and also chloride ions are released. Under conditions of equimolar mixture of hypochlorite to ammonia, N2 is the product, but too large an excess of reagents in the relation 2:1 (Cl:N) results in the oxidation of NH_3 to nitrates. In practice the additive is applied in 1.0 to 1.5 molar excess relative to ammonia. A larger excess of reagents is used if the ash has higher carbon content or lower than the optimum pH value. Reaction proceeds according to the equation:

$$2NH_3 + 3ClO^- \rightarrow N_2 + 3Cl^- + 3H_2O \tag{15}$$

Table 3 shows the experimental results obtained. Calcium hypochlorite has been preliminarily dissolved in water and sprayed in the form of a mist to ash and then mixed.

Table 3. Oxidation efficiency and ammonia removal data [18]

Proportion of reagents (Cl:N)	Addition of calcium hypochlorite [kg/t]	Moisture content(%)	Final NH$_3$ content (ppm)	Reaction efficiencyNH$_3$(%)
0.0:1.0	0	0	500	0
0.5:1.0	1.81	1	300	40
1.0:1.0	3.62	2	30	94
1.5:1.0	5.44	3	20	96
2.0:1.0	7.26	4	15	97

The ammonia removal depends on: the pH of the ash, the process temperature, the process time, the amount of reagent, and the amount of reducers (in the ash) which can slow down the reaction [18]. It is proposed to use two methods depending on the moisture of ash: dry mixing (dry ash) – the reagent is activated by the addition of water and then in its active form reacts with ammonia or wet mixing (wet ash) –occurs more rapidly, a good mixing of the components is necessary. In practice, systems in the United States process ash containing of NH$_3$ at the 75–300 ppm level, using 1–1.4 kg of calcium hypochlorite per 1 ton of ash. Technologies are adapted to operate in the range of 0–2.7 kg of calcium hypochlorite per 1 ton of ash, depending on its quality. The reported costs of running the installation with a capacity of 150 ton/h is less than $500 000, and the building time of the installation is 6 to 9 months (according to data for 2005) [18].

The advantages of the ASM technology:

- ▶ the small amount of reagent used,
- ▶ the small investment and low maintenance costs,
- ▶ two variants of the process: dry or wet, depending on the destination of ash,
- ▶ the cost of the reagent can be minimized by using technology equipped with the "on demand" option. Then the ash is cleaned when necessary.

The disadvantages of ASM technology:

- ▶ license fee,
- ▶ the addition of excess calcium hypochlorite can cause difficulties with the ashes,
- ▶ usage if dry calcium hypochlorite because of its strong oxidizing properties (constituent of explosive mixtures) carries the obligation to comply with stricter safety standards and regulations,
- ▶ usage of wet method generates additional energy and costs,
- ▶ it is not specified how to prevent corrosion caused by calcium hypochlorite and its impact on the life of the installation, which does not preclude the need for additional corrosion protection.

3.3. Catalytic methods of conversion of ammonia to nitrogen

Selective catalytic oxidation (SCO) of ammonia to nitrogen based on reaction (17) [19, 20]:

$$4\,NH_3 + 3O_2 \rightarrow 2N_2 + 6\,H_2O \tag{17}$$

For the catalytic activity in this process, we can use e.g.: CuO, Fe_2O_3, Co_3O_4, MnO_2, MoO_3, V_2O_5, CuO/La_2O_3, CuO/RuO_2. The main problem is to obtain good selectivity with respect to nitrogen. More recently, catalyst systems have been proposed were oxides of Mg-Cu-Fe are formed from the precursor, a hydrotalcite $(Mg_6Al_2(CO_3)(OH)_{16}.4(H_2O))$ [20, 21]. The best obtained results are: 60% conversion rate of the ammonia to N_2 with a selectivity of over 90% at 450°C for the composition of the inlet gas: 0.5% ammonia, 2.5% oxygen, 97% of inert gas [20, 21]. The publication indicates that the catalyst is resistant to water vapour, however, it doesn't show the information about the sensitivity to SO_2. The SCO process using these catalysts can be carried out in the temperature range of 300–450°C. At a laboratory scale, with gas flow of 40 ml/min and the amount of catalyst 100mg no significant decrease in the conversion extent to GHSV 61600h-1 catalyst loading was observed. There are two reaction paths within the SCO. The first two-step reaction "in situ" (18, 19) [19, 20]:

$$4NH_3 + (3+2x)O_2 \rightarrow 4NO_x + 6H_2O \tag{18}$$

$$3NO_x + 2xNH_3 \rightarrow (x+1.5)N_2 + 3xH_2O \tag{19}$$
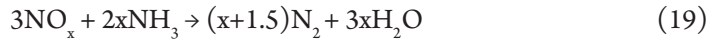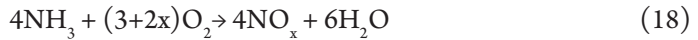
The second is based on $\cdot NH_2$ radical formation, with the intermediate stage comprising hydrazine formation (20–23) [19,20]:

$$NH_{3(g)} \rightarrow NH_{3(ads)} \tag{20}$$

$$NH_{3(ads)} \rightarrow \cdot NH_{2(ads)} + H^+ + e^- \tag{21}$$

$$2\cdot NH_{2(ads)} \rightarrow N_2H_{4(ads)} \tag{22}$$

$$N_2H_{4(ads)} \rightarrow N_2 + 4H^+ + 4e^- \tag{23}$$

The advantage of selective oxidation of ammonia is the ability to eliminate it, prior to separation of the ash from the exhaust gas, while the necessity of the catalysis is the disadvantage. Then the problem might be catalyst poisoning in the presence of components such as SO_2 or some of the heavy metals present in the ash, such as As, Hg, Pb. However, no detailed information has been found about thelifespan of catalysts used in the process. The license fee for the implementation of the technology will increase investment costs [19, 20].

In addition, a copper/titanium dioxide catalystis proposed, which works well at lower temperatures (95% conversion rate of the ammonia at a temperature of 250°C with a oad of catalyst GHSV = 50 000h^{-1}. The reaction selectivity to nitrogen is above 93% at temperatures up to 350°C [19, 20]. The problem concerning the catalytic process is the leaching of the catalyst bed with the flue gas contaminated with ash. A scheme for the mechanism of selective oxidation of ammonia to nitrogen over a Cu/TiO_2 is shown in Figure 1 [19, 20].
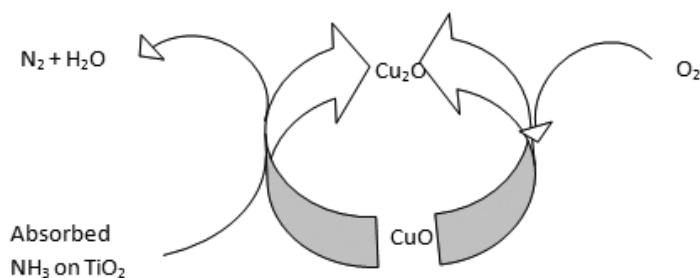
Fig. 1. Illustration of the mechanism of selective oxidation of ammonia to nitrogen over a Cu/TiO_2 [19, 20]

On the other hand, another catalyst system is described by the authors of publication [21]. The study involved Cu–SSZ-13 (a new, more robust and active small-pore Cu-exchanged chabazite (CHA; SSZ-13 and SAPO-34) zeolites have been recently commercialized, in this paper we explore the effect of using Cu–SSZ-13 as the SCR component of the ASC) and Pt/Al_2O_3 in several variants. Reactions on catalysts are described by the reaction equations (18, 19). The catalysts were tested in: pure form, dual-layer catalysts, where dual-layer catalysts comprised a Cu–SSZ-13 top layer and a Pt/Al_2O_3 base layer and mixed layer. In each embodiment, the catalyst has the form of monoliths with a cell density of 400 cpsi and dimensions of 1 in. diameter and 3 in. length. These were cut into 2 or 0.5 cm long, ∼0.8 cm diameter samples, and were coated by dipping the monolith. Tested catalysts are shown in Table 4.

Table 4. etailed description on monolith catalysts used [21]

Samplename	Pt loading (g/ft³ monolith)	Pt/Al_2O_3 loading (g/in³ monolith)	Cu–SSZ-13 loading (g/in³ monolith)
Pt(3)	2.7	1.4	0
Cu–SSZ(1.5)	0	0	1.5
CuZ(0.85)Pt(3)	2.8	1.4	0.85
CuZ(1.5)Pt(3) - a	2.6	1.3	1.5
CuZ(1.5)Pt(3)_high - b	2.5	1.3	1.5
CuZ(3)Pt(3)	2.8	1.4	3
Hybrid - c	2.7	1.4	2.2

a – Dual layer and mixed catalysts.
b – Cu wt% in Cu–SSZ-13 used ∼5.71.
c – 0.7 g/in³ of Cu–SSZ-13 coated on top of mixed CuZ(1.5)Pt(3).

The prepared catalyst was placed in a tubular reactor and subsequently treated using three different gas mixtures. First; Cu-SSZ-13, 500 ppm NH_3, 375 ppm NO, 125 ppm NO_2, 5% O_2, 2.5% H_2O, 2% CO_2, bal. Ar. GHSV= 66k h⁻1; second; Cu-SSZ-13, 500 ppm NH_3, 375 ppm NO, 125 ppm NO_2, 5% O_2, 2.5% H_2O, 2% CO_2, bal. Ar. GHSV= 265k h⁻1; Third; Cu-SSZ-13, 500 ppm NH_3, 500 ppm NO, 5% O_2, 2.5% H_2O, 2% CO_2, bal. Ar. GHSV= 265k h⁻1. Figures 2,3and 4 show the results obtained for the Cu-SSZ-13 [21].

For the first test the maximum NH_3 conversion was 94% at 300°C. For the second and third test while increasing the volume flow rate, the degree of conversion decreased, as seen in Figures 2 and 3 [21].

Figure 5 (a, b, c, d) shows the results of the tests of the catalysts described in Table 4. The highest selectivity of 90% relative to the N_2 is given by catalyst CuZ(1.5)Pt(3) and CuZ(3)Pt(3)_high at 375°C. The authors also describe the effect of the content of individual elements on the catalytic activity of the catalysts used [21].
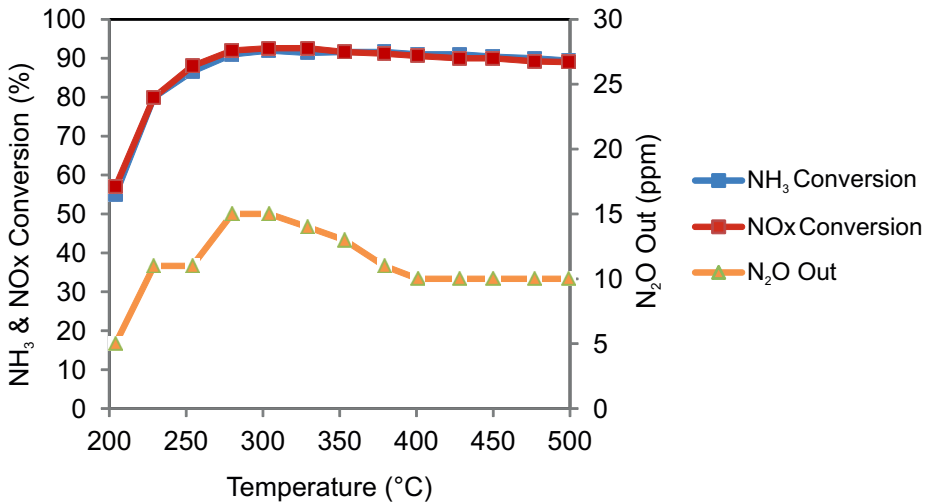

Fig. 2. Catalyst: Cu-SSZ-13, 500 ppm NH_3, 375 ppm NO, 125 ppm NO_2, 5% O_2, 2.5% H_2O, 2% CO_2, bal. Ar. GHSV= 66k h⁻¹[21]
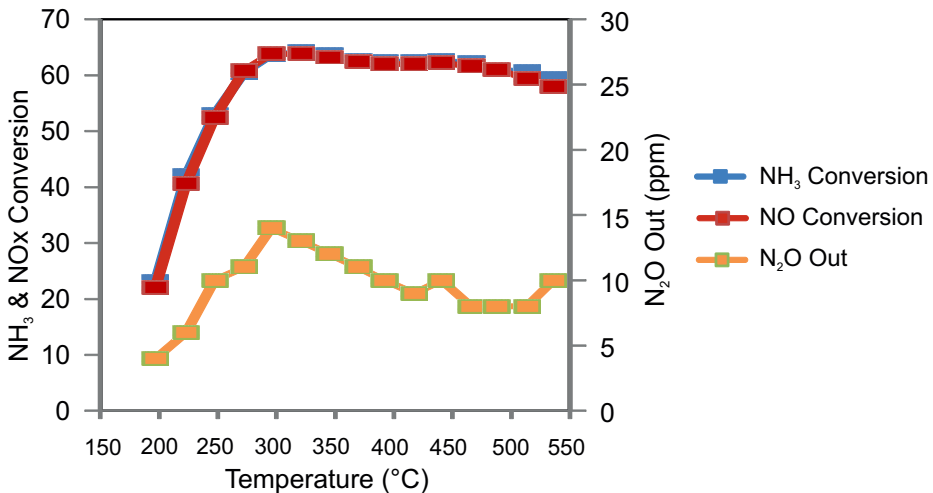

Fig. 3. Catalyst: Cu-SSZ-13, 500 ppm NH_3, 375 ppm NO, 125 ppm NO_2, 5% O_2, 2.5% H_2O, 2% CO_2, bal. Ar. GHSV= 265k h⁻¹[21]
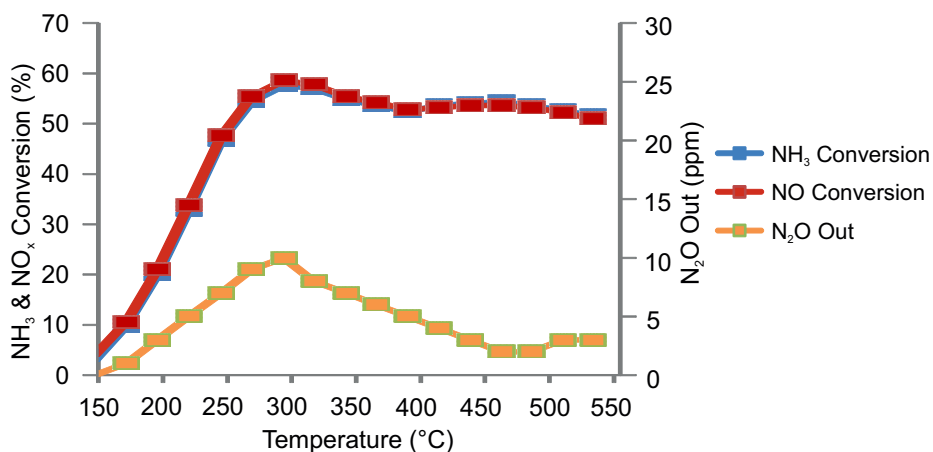
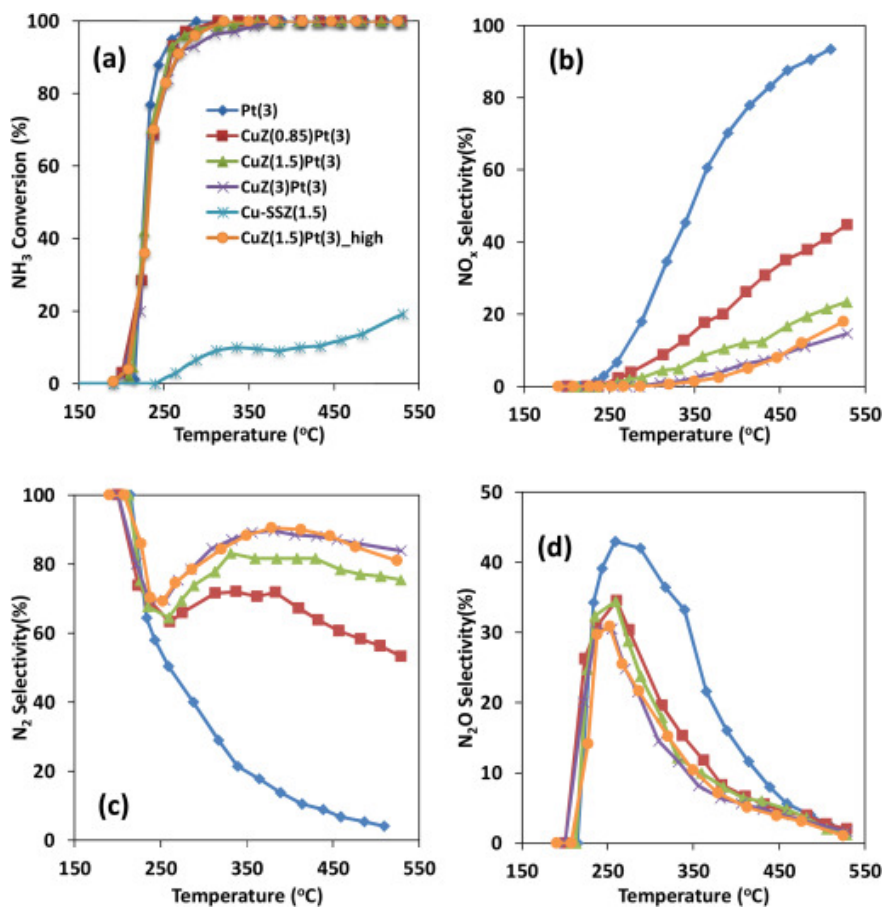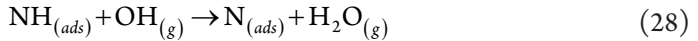Fig. 4. Catalyst: Cu-SSZ-13, 500 ppm NH_3, 500 ppm NO, 5% O_2, 2.5% H_2O, 2% CO_2, bal. Ar. GHSV= 265k h^{-1}[21]
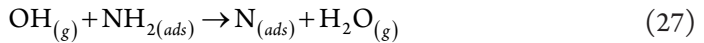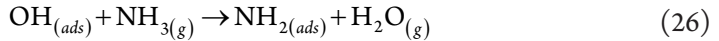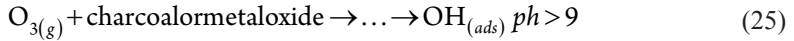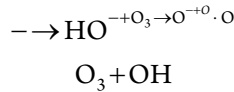

Fig. 5. Research of catalysts (a) NH_3 conversion, (b)NO_x selectivity, (c) N_2 selectivity (d) N_2O selectivity; 500 ppm NH_3, 5% O_2, 2.5% H_2O, 2% CO_2 and GHSV=66 k h^{-1}[21]

43

3.4. Ash ozonation

According to the literature [21] fly ash can act catalytically on the process of oxidation of ammonia with ozone atroom temperature (23^0C). Tests were carried out using a fixed bed reactor. The aim of the research was to investigate the catalytic properties of fly ash with a constant ammonia content ($11ppm_v$) This led to efficiency between 35–60% of ammonia conversion at a starting concentration about 11ppm by volume, and the ozone concentration in the range of 62 to 866 ppm by volume. The catalytic activity of the ash slightly depends on their origin. The best results obtained by the authors are:

▸ 45% degree of conversion of ammonia, the ammonia content of the initial 11 ppmvol; residence time 0.34s; an ozone concentration of 62 ppmv.; amount of ash in the bed 5 g;
▸ The content of formed nitrogen dioxide does not exceed 3%.

The potential reaction mechanism is as follows (reactions 24–29):

$$
\begin{aligned}
&3 \\
&3 \\
&+ \rightarrow HO_3 \rightarrow OH \\
&\quad - + H \\
&- \rightarrow HO^{-+O_3 \rightarrow O^{-+O} \cdot O} \\
&O_3 + OH
\end{aligned}
\tag{24}
$$

$$O_{3(g)} + charcoalormetaloxide \rightarrow \ldots \rightarrow OH_{(ads)}\ ph>9 \tag{25}$$

$$OH_{(ads)} + NH_{3(g)} \rightarrow NH_{2(ads)} + H_2O_{(g)} \tag{26}$$

$$OH_{(g)} + NH_{2(ads)} \rightarrow N_{(ads)} + H_2O_{(g)} \tag{27}$$

$$NH_{(ads)} + OH_{(g)} \rightarrow N_{(ads)} + H_2O_{(g)} \tag{28}$$

$$2N_{(ads)} \rightarrow N_{2(g)} \uparrow \tag{29}$$

All phases could initiate adsorption/reaction with ozone. In the use of char the authors speculate that it is primarily carbon that interacts with O_3 - meanwhile metals could also be present on the char surface, due to the presence of ash in the original biomass. The general consensus in the literature is that ozone dissociatively adsorbs onto metal oxides (Mn, Co, Cu, Fe, Ni) forming active oxygen species (O, ·OH). Additionally was observed that gas humidification favours the process [21].

The authors of the patent [22] provide experimental data of ammonia oxidation by ozone. The process was conducted by applying water to the ash in the form of a mist or warm humid air, constituting 1–5 wt-% moisture in the solid ash. Under these conditions, in the so-called water fog method was implemented using a mixture of ozone, air with ozone, oxygen with

ozone, and oxygen with 30% hydrogen peroxide as a co-oxidizing agent (co-oxidant), as a source of fog. All the results of the methods which used ozone with dry or semi-dry ash (1–5% water) are shown in Table 5. In all variants of the process, pH should be increased (pH > 10) by using an addition of $Ca(OH)_2$ [22].

Table 5. Resultsof ozonation by O_2 or O_3 [22]

Oxidizing agent	Final content of NH_3 (ppm)*
O_2 (150°C)	1200
O_3 4000 ppm (20°C)	850
O_3 4000 ppm (150 ˚C)	500
O_3 2 % obj. (150°C)	400

* initial concentration NH_3 at 1200 ppm.

Ozone reduces the ammonia content in all the conditions used, and the best results were obtained for an ozone concentration at a level of 2% by volume and process temperatures of 150°C [22].

3.5. Methods of wet and semi-dry ammonia leaching

3.5.1. Ammonia absorption with the modified turbulent scrubber usage

Studies were performed using an exhaust gas scrubber containing fly ash and operating in batch mode. Exhaust gases are introduced into the water by a thin gap, and then through the use of multiple baffles a highly turbulent flow of the gas-liquid mixture was obtained. This approach allows single step removal of fly ash to a hydraulic diameter to 0.5 microns) and a water-soluble gases such as ammonia [23–25].
Key features of the resulting solutions are:

▸ Maximum efficiency of removal of ammonia (79%) was obtained with a gas initially containing 45 ppm by volume of ammonia at a flow rate of 3.5 m³/min; the water level in the apparatus was 60 cm;
▸ Maximum efficiency of removal of fly ash (62.48%) is achieved for particles having a diameter of 0.25 microns with a mass flow rate of the exhaust gas ratio of 140 mg/min; volumetric flow rate of the exhaust gas 3.5m³/min, the water level in the apparatus 58 cm,
▸ The maximum recorded pressure drops in the flow (150 mm H_2O) was obtained for volumetric flow rate 4.5m³/min and the water level in the apparatus 60 cm.

In the cited publication there were no design guidelines for increasing the scale of operations. Tests were carried out at room temperature. In the case of continuous mode of operation, a second apparatus –a filtration device – would be required. Other problems will be wastewater containing traces of heavy metal and vibrations generated during operation (due to the strongly turbulent flow) [23–25].

3.5.2. Humid air in a stationary or fluidized bed

There is also a process proposed in which the fly ash is in contact with a humid air in a stationary or fluidized bed. Parameters used at lab scale [23–25]:

- ▶ Gas distributor: porous glass 0.15–0.18 mm,
- ▶ Reactor diameter of 25 mm,
- ▶ Flow of moist air of 0.9–0.8 l/min,
- ▶ The amount of ash 10 g.

However, the required time contact (on the order of several hours) precludes usage. In the cited work the use of so-called atomized mist in form of suspended micro droplets of water has also been proposed. The dispersion of water in the air was obtained using an ultrasound device. In this case, at a contact time of five minutes the ammonia content was reduced from 950 ppm to about 250 ppm. Measurements were carried out in batch mode in which each phase of wetting or drying the ash lasts about 10 minutes. A disadvantage of the system may be that more moisture will cause ash particle agglomeration which leads to an increase in flow resistance in the fluidized bed. Furthermore, hydrogen peroxide has been proposed as the oxidizing agent [23–25].

3.6. The release of ammonia to the water from fly ash

Studies show that ammonium sulphate and ammonium interact strongly enough with the surface of the ash to make the release of ammonium ion much slower than the expected rate of dissolution in the water. Despite this, after a period of about 10 minutes, about 85% of ammonia was released from the ash into the water [23–25].

4. Thermalmethods

It is known from thermogravimetry studies that the temperature profile of ammonia release depends on the composition of the fly ash, which also indicates that ammonia is not present in the pure form of sulphate and bisulphate [32]. Typically, the release of ammonia from the ash takes place at a higher temperature than the thermal decomposition of pure ammonium sulphate (in the cited studies ammonia release temperature was 390°C for ash and 210°C for pure ammonium sulphate). It is also known that ammonia can be adsorbed on the active centres of acidic aluminium silicate in the ash. There are temperature profiles of ammonia release from the ashes available, obtained from the SCR and SNCR processes. In the case of SNCR release of ammonia was observed in the temperature range 200–400°C, in the case of SCR in the range of 320–480°C [28–35].

4.1. Carbon Burn-Out technology

Burning of carbon residue and thermal decomposition of ammonium sulphate and ammonium bisulphate has been proposed. The process is conducted in a fluidized bed reactor at a temperature of about 700°C with a residence time of 45 minutes. As a result of

this process ash content of less than 5 ppm ammonia is obtained. In addition, the ash has higher pozzolan activity and improved performance (lower TOC). The inventor of the ash technology is Progress Materials Inc., with the support of members of EPRI. Commercial installations of CBO™ include the Wateree Station of South Carolina Electric and Gas (1999, two units, process 180,000 tons per year of ash with an average of 12.5% LOI) and Winyah Station of Santee Cooper (2002; 200,000 tons of fly ash peryear) [26, 27].

4.2. ERC Technology (Energy Research Center)

It proposes a process in which the fly ash from the silo is introduced into the fluidized bed and fluidized by heated air. The release of ammonia begins at 150°C. The process is carried out with a continuous flow through the bed ash. Agglomerates of fine-grained fraction are broken down by the application of acoustic waves generated by speakers emitting sound waves of high intensity. Studies were conducted in terms of the ammonia content of 500 to 1000 ppm. It is also possible to modify the system by installing an additional electric heater (submerged in the bed). When using this method it is also necessary to install additional ash coolers –heat exchangers – at the end of the bed. The use of sound waves requires an analysis of the mechanical energy transfer efficiency as well as the transmission of vibrations of selected frequency to other parts of the apparatus in the vicinity of the installation [33, 34].

Advantages of ERC [33]:
- ▸ no need for additional resources,
- ▸ relatively easy scaling of installations operating in a continuous mode,
- ▸ no energy inputs for subsequent drying of ash,
- ▸ no investment in additional equipment (dryers, filtration, trays of raw materials),
- ▸ relatively low process temperature 343–398°C,
- ▸ the ability to remove up to 90% of ammonia absorbed in the ashes.

Disadvantages of ERC [33]:
- ▸ technology dedicated to BFB fluidized bed boilers, in which the waste gases must be above the bed as long as possible,
- ▸ technology developed at laboratory scale, lack of experience in production scale,
- ▸ need to ensure a constant flow of exhaust gas stream,
- ▸ needof fluidized bed equipped with a sound system preventing agglomeration of the bed.

4.3. Other thermal methods

Compared to other options, the advantage of processes based on thermal desorption at 300–450°C is mainly the small investment cost. In this case, it is necessary to provide thermogravimetric analysis to determine the conditions of the process. The ERC method has so far only been used for ashes with a high ammonia content (> 500 ppm) and no data are available on its effectiveness for ashes with lower ammonia content (but exceeding the maximum allowed level)[28–35].

5. Conclusions

Analysis of the cases associated with the presence of ammonia in ashes indicates that this is a direct consequence of the denitrification –catalytic and non-catalytic selective reduction (SCR, SNCR) of flue gases. The excess of ammonia used in these methods passes in unreacted form to the fly ash impairing its properties and thus affecting the quality of the final solid product. This bounding occurs due to the presence of acidic functional groups on ash particles surface which increase ammonia attachment. Ash neutralization with a base cause immediate emission of NH_3 to the environment. The optimal process that can be applied should be able to reduce the total ammonia content to less than 100 ppm in the dry ash.

Despite the variety of methods presented, it is difficult to choose a method that could be implemented in the energy market without additional modifications. For all methods, the imperfections of the applied technologies may bring investment and operational costs that should be taken into account. Additional costs are also generated by licenses for a patent covering the technology. When choosing the right technology it is necessary to consider economic aspects, production capacity and chemical composition of processed raw material as well as final product application.

References

[1] Zamorowski K., *Aspekty dostosowania energetyki krajowej do standardów emisyjnych tlenków azotu – wpływ zastosowanych technologii na pracę kotła oraz koszty realizacji odazotowania spalin*, „Energetyka" nr 6/2013,

[2] Wadrak P., *Proces inwestycyjny oraz Metody Redukcji NOx, SOx na przykładzie wybranych polskich obiektów energetycznych, Nowoczesna Energetyka Europy Środkowo-Wschodniej*, 2015.

[3] Directive 2010/75/EU of 24 November 2010 on industrial emissions (IED), The Minister of Environment of 22 April 2011. On emission standards from installations, OJ No. 95, item. 558.

[4] Brendel G.F., Bonetti J.E. et al., *Investigation of Ammonia Adsorption on Fly Ash Due to the Installation of Selective Catalytic Reduction Systems*, Technical Report.,West Virginia University Research Corp., 2000

[5] O'Connor, D., Behavior of Ammoniated Fly Ash: Effects of Ammonia on Fly Ash Handling, Disposal, and End-Use, EPRI, Palo Alto, CA: 2002, Technical report no. 1003981

[6] Gąsiorowski S.A., Bittner J., Hrach F., *Removing from Fly Ash, Separation Technologies*, LLC 101 Hampton Avenue, Needham, Massachusetts, USA, 2015.

[7] Gąsiorowski S.A., Hrach F.J., Method for Removing Ammonia from Ammonia Contaminated Fly Ash, Patent US6077494, 2000.

[8] Szponder D., *Badania wybranych właściwości popiołów lotnych z zastosowaniem analizy obrazu*, PhD thesis, AGH, 2012.

[9] Sikora T., Nowak P., *Raport z inwentaryzacji popiołów lotnych*, DBAA/13-901/3370, Research & Development Division, EDF Poland, September 2015[internal publication of EDF Polska].

[10] O'Connor D., *Ammonia Removal from Fly Ash: Process Review – Separation Technologies LLC (ST) – Ammonia Removal Process*, EPRI, Palo Alto, CA: 2007: 1012697, www.epri.com (access: 28.06.2015).

[11] Kulaots I., Gao Y-M., Hurt R.H., Suuberg E.M., *Adsorption of Ammonia on Coal Fly Ash*, International Ash Utilization Symposium, Center For Applied Energy Research, University of Kentucky, 2001.

[12] Czekaj M., Czupryński P., *Podsumowanie wiedzy w Grupie EDF Polska i EDF Polska R&D w zakresie zjawiska „poślizgu amoniaku" po instalacjach deNOx*, DBAA/10-911/3301, Research & Development Division, EDF Poland, May 2014 [internal publication of EDF Polska].

[13] Zhao Y-l., Yang W., Zhou J., et.al., *Experimental study on ammonia adsorption by coal ashes*, "Journal of Fuel Chemistry and Technology", Vol. 43(3), 266–272.

[14] Ma Z.B., Bai Z.Q., Bai Jet.al., *Evolution of coal ashwith high Si/Al ratio under reducing atmosphere at hightemperature*, "Journal of Fuel Chemistry andTechnology", 40(3), 2012, 279–285.

[15] Gao Y.M., Külaots I., Chen X., et.al., *The effect of solid fuel type and combustion conditions onresidual carbon properties and fly ash quality*, Proceedings of the Combustion Institute, 29(1), 2002, 475–483.

[16] Gąsiorowski S.A., Bittner J., Hrach F., *Removing from Fly Ash, International Ash Utilization Symposium*, Center For Applied Energy Research, University of Kentucky, 2001.

[17] Ziegler, SD., Bittner, J, *Fly Ash Carbon Separation and Ammonia Removal in Florida*, IEEE-IAS/PCA Cement Industry Technical Conference (CIC), 2013.

[18] Ammonia Removal from Fly Ash: Process Review, Headwaters Ammonia Slip Mitigation (ASM™) Technology (www.epri.com), EPRI Project Manager D. O'Connor, Technical Update, 2005.

[19] Shilong He, ChangbinZhang, Min Yang, YuZhang, WenqingXu, Nan Cao, Hong He, "Separation and Purification Technology" 58, 2007, 173–178.

[20] Chmielarz L., Węgrzyn A.,Wojciechowska M., Witkowski S., Michalik M., *Selective Catalytic Oxidation (SCO) of Ammonia to Nitrogen over Hydrotalcite Originated Mg–Cu–Fe Mixed Metal Oxides*, Catalysis Letters, 141(9), 09/2011, 1345–1354.

[21] Shresthaa S., Harolda M.P., Kamasamudramb K., Kumarb A, Olssonc L., Leistnerc K., *Selective oxidation of ammonia to nitrogen on bi-functional Cu–SSZ-13 and Pt/Al2O3 monolith catalyst*, "Catalysis Today" 267, 2016, 130–144.

[22] Kastner R.J., *Catalytic ozonation of ammonia using biomass char and wood fly ash*, "Chemosphere" 75, 2009, 739–744.

[23] Mehta A.K., Hurt R.H., Gao Y., Chen X., Suuberg E.M., *Dry and Semi-dry methods for removal of ammonia from fly ash*, Patent US6746654 B2, 2004

[24] Wang H., Ban H., Golden D., Ladwig K., *Ammonia release characteristic from coal combustion fly ash*, "Fuel Chemistry Division Preprints", 47(2), 2002, 810.

[25] Cardone C., Kim A., Schroeder K., *Release of ammonia from SCR/SNCR fly ashes*, World of Coal Ash (WOCA), April 11–15, 2005.

[26] Keppeler J.G., Carbon Burn-Out, *Commercialization and Experience Update*, http://www.pmiash.com/cbo/acaa01paper.html, 2009 (access: 30.06.2016).

[27] Kirkconnell S.F., P.E. and J.G. Keppeler, P.E., *Carbon Burn-Out™ – A State of the Art in Commercial Ash Beneficiation*, PMI Ash Technologies SVP named new American Coal Ash Association Chair, May 2007.

[28] Czekaj M., Kulesz E., Jura K., *Zawartość amoniaku w popiele – analiza ryzyka związanego z zastosowaniem popiołów oraz wskazanie możliwości modyfikacji instalacji odpopielania*, Report DBAA/10-911/3002, Research & Development Division, EDF Poland, October 2012 [internal publication of EDF Polska].

[29] Górecka T., *Określanie kinetyki uwalniania się amoniaku z popiołów lotnych po uruchomieniu instalacji odazotowania*, Report no 271/703/12, ZWP Emitor, July-September, 2012.

[30] Rubel A.M., *Forms of ammonia on SCR, SNCR and FGC combustion ashes*, "Fuel Chemistry Division Preprints", 47(2), 834, 2002.

[31] Y.M. Gao, X. Chen, G. Fujisaki, A. Mehta, E.M. Suuberg and R.H. Hurt, *Dry and Semi-Dry Methods for Removal of Ammonia from Pulverized Fuel Combustion Fly Ash*, "Energy and Fuels" 16, 2002, 1398–1404.

[32] Rubel A.M., Rathbone R.F., Stencel J.M., T*hermal Characteristics of Ammonia Release from Combustion Ash*, International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, 2001.

[33] Conn R., Sarubac N., Levy E., *Removing ammonia from fly ash*, "Lehigh energy update", Vol. 19(2), June 2001, http://www.lehigh.edu/~inenr/leu/leu_28.pdf%5D. (access: 10.09.2015).

[34] Lawton K.B, *Ammonia removal from fly ash using a continuously operating acoustically assisted fluidized bed*, Theses and Dissertations, Lehigh University, 2002, 733.

[35] Lawton K.B., *ERC Completes development of technique for removing ammonia fr om fly ash, Lehigh energy update*, Vol. 20(1), 2002, http://www.lehigh.edu/energy/leu/leu_32.pdf (access: 10.09.2015).