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Possibilities of elimination of ammonia slip from technological water in power plants

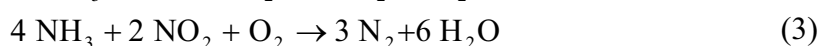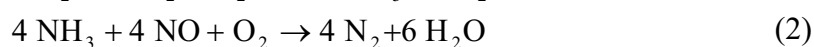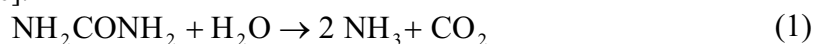**J Hajzler[1], T Opravil[1], J Pořízka[1] and P Ptáček[1]**

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Abstract. The purpose of this study is to find new possibilities of elimination or separation of ammonium compounds from technological water produced by powerplants and incinerators, in which the secondary flue gas denitrification methods have been implemented (SCR, SNCR). This paper seeks for a new method of ammonium slip elimination from technological water due to the absence of industrially applicable method and thus fixation of ammonium ions in composite cement eventually in binder containing fly ash. The experiments confirmed the validity of the complex compound utility in given issue. The new method consists in adding a soluble cobalt compound to get an insoluble cobalt complex, the processing conditions were optimized during laboratory testing.

1. Introduction

NO_x, which is contained in flue gas, is composed of NO (90%) and NO_2 (5%). Both gases occur during the combustion process. Primary, relatively harmless, colorless non-drying NO (90–95%) is formed, which reacts with oxygen to form brown, irritating NO_2. The remaining nitrogen oxides are present in very small amounts (5%) and often transform between NO and NO_2 [1]. NO_2 is acid gas that can further react in the atmosphere with OH-radicals to form nitric acid. NO_x contributes to acid rain and eutrophication. To protect human health from the negative effects of NO_x emission limit values (ELV) exist. For waste incineration plants the ELV for NO_x is 200 mg/Nm^3. Primary measures usually do not suffice to reach this ELV, therefore secondary measures must be introduced. The most often used method is selective non catalytic reduction (SNCR). This method is relatively simple and cost-efficient [2, 3]. The principle of the method is the thermal conversion of nitrogen oxides by injecting a reducing reagent into the flue gas stream at an appropriate temperature range, which is known as temperature window [4, 5]. Reducing reagent selectively reacts with nitrogen oxides and converts them into harmless molecular nitrogen and water vapour at relatively high temperatures (850–1100°C) at 0 % O_2 concentration [6, 7]. Ammonia, urea and cyanuric acid are used as the reagent. Under stoichiometric conditions, the chemical process can be written according to equations (1), (2) and (3) [2, 6].

$$NH_2CONH_2 + H_2O \rightarrow 2\,NH_3 + CO_2 \tag{1}$$

$$4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O \tag{2}$$

$$4\,NH_3 + 2\,NO_2 + O_2 \rightarrow 3\,N_2 + 6\,H_2O \tag{3}$$

If the flue gas temperature is too low, NO_x conversion decreases, the reaction rates become very slow and ammonia slip occurs [6]. If the flue gas temperature is above 1100°C, the reaction of NH_3 oxidation becomes predominant (4) [8].

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O \tag{4}$$
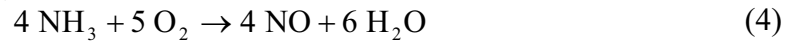
The fate of reducing reagent (ammonia) is shown in Figure 1.
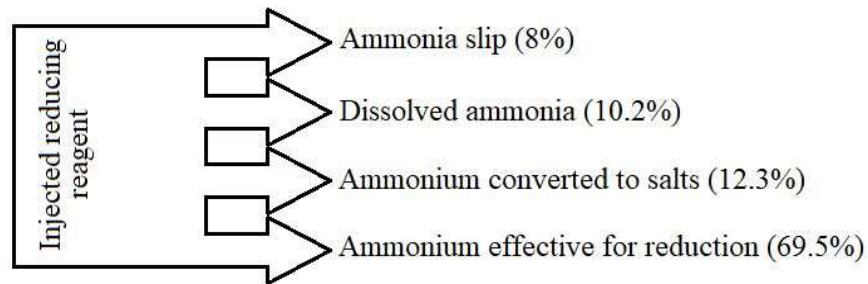
Figure 1. The fate of ammonia.

The SNCR method is usually sufficient to meet the requirement of EVL of 200 mg/Nm³. If, however, the ELV is reduced to 100 mg/Nm³, as it is already the case in some regions in Germany [9], the SNCR method might not be suitable to meet this ELV, because the removal efficiency is about 50%. In that case, the method of selective catalytic reduction (SCR) is an interesting alternative, because the removal efficiency is up to 90% and it would be the tail end solution of the problem [2, 10]. In SCR the reduction reagent reacts with nitrogen oxides on a $TiO_2/V_2O_5/WO_3$ catalyst surface, at the temperature range between 220–350°C [1]. However, the installation, operation and maintenance costs are noneffective. The installation of SNCR system makes just 20–35% of the cost of the SCR system [11]. But there is another obstacle regarding the environment. Using the SCR method instead of the SNCR method direct environmental impact (reducing NO_x) in the impact categories acidification or eutrophication is reduced. Unfortunately SCR involves higher indirect environmental impacts than SNCR, mainly due to the need to reheat the combustion gas burning fuel oil in already existing facilities with SNCR. When fuel oil is used as an energy source to reheat the flue gas, these indirect impacts are higher than the impacts directly avoided by lower NO_x emissions. Those indirect impacts have an influence on global warming. From that reason, the optimization of SNCR should be preferred to installing the tail end SCR in existing installations. For new installations, where the space to locate the catalyst after the boiler is available, avoiding the need to reheat the combustion gas could be an alternative for SNCR [2].

Even if the temperature window is kept in the SNCR system, the formation of ammonia slip occurs, which is the result of incomplete reaction of NO_x with the reduction reagent. Ammonia slip results in several problems, including ammonium hydrogen sulphate or another ammonia salts formation, which can further cause the corrosion of facility walls. The absorption of ammonia by fly ash may prevent its further use. Apart from ammonium hydrogen sulphate also huge amount of another soluble ammonium salts, such as sulphates, nitrates, chlorides, are contained in ammonia slip [12].

The problem is that almost all ammonium salts are well soluble in water, but an insoluble complex compound ammonium hexanitrocobaltate was found. This ammonium complex is formed very quickly when ammonium ions react with soluble sodium hexanitrocobaltate, which is yellow brown crystal well soluble in water and insoluble in alcohols. The water solution is used in analytical chemistry and is known as Fischer salts [13].

The aim of this study is to find a new possibility of elimination of ammonia residues with complex compounds from technological water in the facilities, where high temperature combustion takes place and where secondary denitrification flue gas was introduced. The study focuses on finding a new method, as there is currently no industrially used method, which would solve this problem.

2. Experimental

2.1. Materials
The Portland clinker was ground to 380 m^2/kg (plant Mokrá, CZ). In the experiment, ash (power plant Počerady) was doped with a solution of ammonium hydrogen sulphate (Carl Roth, ≥98,5%, p.a.) in the amount of 30, 50 and 200 ppm and then dried. Sodium hexanitrocobaltate was prepared by the precipitation [14] at Faculty of Chemistry. Gypsum water is water after SNCR. (power plant Počerady).

2.2. Sample preparation
For experiments the agglomerate (mixture of ash and water - transport to the compost) and the stabilizer (ash mixture of lime and energy gypsum) were chosen. According to ČSN EN 197-1, CEM II / B-V paste and mortar were made. The composition of mixtures was designed according to ČSN EN 196-1. The size of beams was 20 × 20 × 100 mm. The composition of each mixture is shown in Table 1. The aqueous extracts were carried out according to ČSN EN 12457-4. Prepared and weighed beams from mixtures after 1, 4 and 7 days were placed in the bottle and then poured with distilled water at the weight ratio 1:10. The bottle was placed in a head-heel shaker for 24 h. The particles were allowed to sediment for 15 minutes. Subsequent filtration was carried out under reduced pressure on a 0.45 μm porous filter.

Table 1. The composition of mixtures.

| Mixture | Clinker [g] | Ash ppm [g] | | | Sand [g] | FGD gypsum [g] | CaO [g] | H_2O [g] | $Na_3[Co(NO_2)_6]$ [mg] |
		30	50	200					
A	0	70	0	0	0	5	3	22	300
B	0	78	0	0	0	0	0	22	300
C	0	78	0	0	0	0	0	22	0
D	455	245	0	0	0	0	0	269.0	55
E	455	0	245	0	0	0	0	261.7	91.5
F	455	0	0	245	0	0	0	206.9	365.5
G	455	245	0	0	2 100	0	0	269.0	55
H	455	0	245	0	2 100	0	0	261.7	91.5
I	455	0	0	245	2 100	0	0	206.9	365.5
J	455	245	0	0	0	0	0	280	0
K	455	0	245	0	0	0	0	280	0
L	455	0	0	245	0	0	0	280	0
M	455	245	0	0	2 100	0	0	280	0
N	455	0	245	0	2 100	0	0	280	0
O	455	0	0	245	2 100	0	0	280	0

2.3. Methods
The filtered extract was analyzed by means of inductively coupled plasma emission spectroscopy (ICP-OES). In this work the ICP-OES method was performed using the ULTIMA 2 instrument from HORIBA Scientific. An ion chromatography (IC) method was used to determine the ions in analyzed solutions. The IC method was performed using Metrohm's 850 Professional IC. The water to binder ratio (w/b) was set to 0.4. It is the ratio between the total amount of water (g) and the total amount of binder (g), which is the sum of amounts of ash and clinker.

3. Results and discussion

Sodium hexanitrocobaltate was used to reduce the ammonium ions contained in the sample of gypsum water. It was found that ammonium hexanitrocobaltate was formed, which precipitated and rapidly settled in the solution. The formation of ammonium hexanitrocobaltate was proceeded according to the equation (5). [14] The first experiment was performed with the sample of gypsum water. The determined contents of selected substances in gypsum water are given in Table 2.

$$3\,NH_4^+ + Na_3\left[Co\left(NO_2\right)_6\right] \rightarrow \downarrow \left(NH_4\right)_3\left[Co\left(NO_2\right)_6\right] + 3Na^+ \tag{5}$$
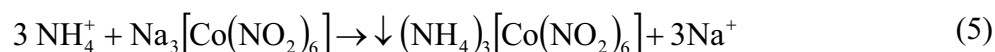
Table 2. Analysis of gypsum water using ICP - OES and IC methods.

Component [mg·l^{-1}]					
SO_4^{2-}	sulphates	16 404.30	Ni	nickel	3.94
Cl^-	chlorides	7 054.56	Zn	zinc	3.86
NO_3^-	nitrates	5 566.86	Cu	copper	2.35
Na^+	sodium ion	5 462.80	Co	cobalt	1.78
ρ_N	total ammonium nitrogen	2 835.45	Al	aluminium	0.25
Mg^{2+}	magnesium ion	1 701.30	Cr	chrome	0.21
K^+	potassium ion	920.9	Cd	cadmium	0.11
Ca^{2+}	calcium ion	696.23	As	arsenic	0.03
F^-	fluorides	80.57	NO_2^-	nitrite	-*
Fe	iron	8.36	Pb	lead	-*

*These components were below the detection limit
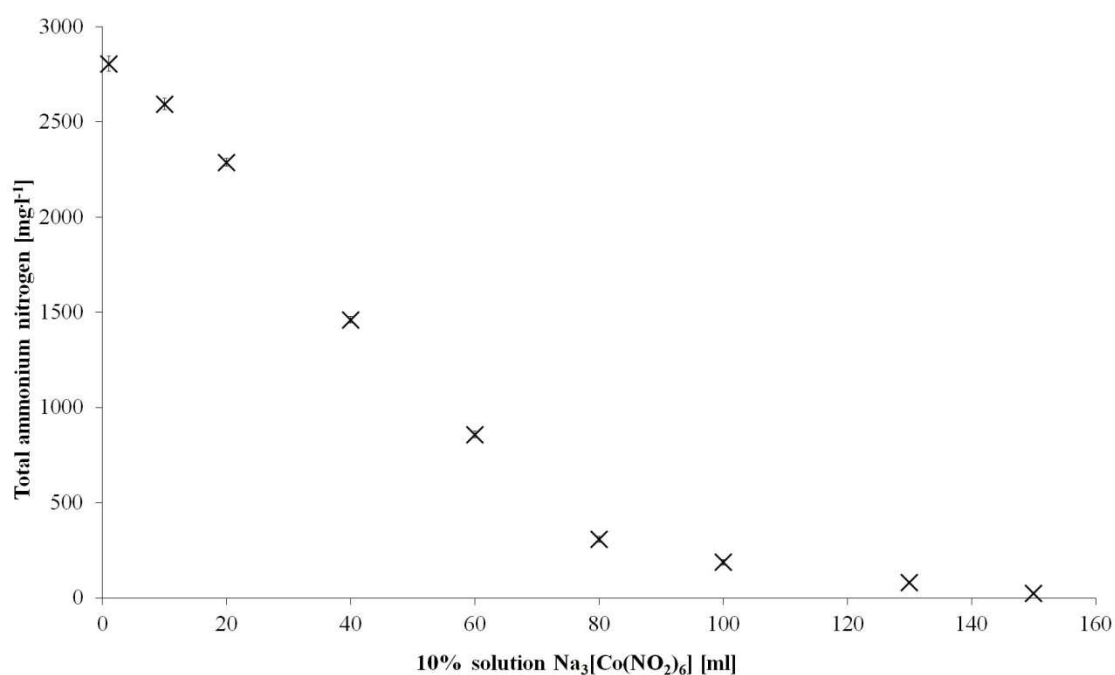
Figure 2. Dependency of total ammonium nitrogen on the addition of coordination complex into gypsum water after 10 minutes.
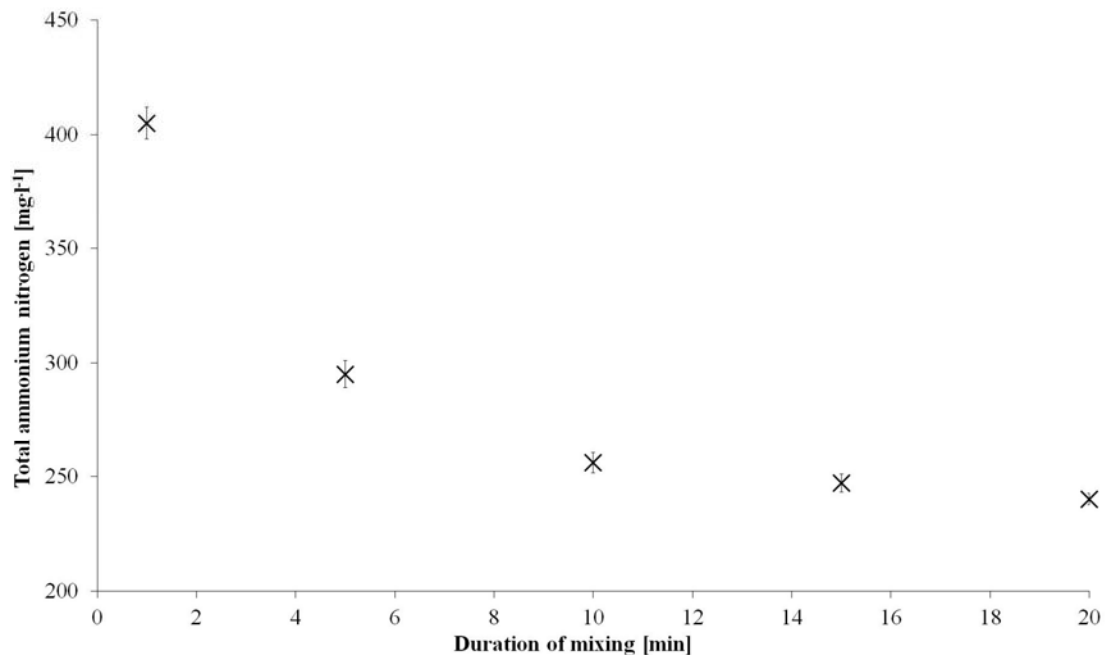
Figure 3. Dependency of total ammonium nitrogen the on duration of mixing in gypsum water.

The precipitate was subjected to XRD analysis. The measured spectrum was compared to the database and it was confirmed that the precipitate was indeed ammonium hexanitrocobaltate. Figure 2 shows the trend of total ammonium nitrogen (TAN) in gypsum water decrease with increased addition of 10% water solution of sodium hexanitrocobaltate. Sodium hexanitrocobaltate reduces the ammonium ions present in the sample. The sodium ion is partially substituted by ammonium in the compound. (For detailed description the NMR analysis should be beneficial). This results in the formation of insoluble and stable ammonium hexanitrocobaltate, which precipitates from the solution and quickly settles. The influence of duration of mixing on the TAN decrease in the analyzed sample was further studied and is shown in Figure 3. From the figure it can be seen that with increasing stirring time, the content of TAN in the sample decreases. The amount of nitrogen clearly decreases when being stirred within the first 10 minutes, with longer stirring, the amount of nitrogen in the sample decreases slowly. Hence, 10 minutes of mixing is sufficient time to remove TAN from the sample. On an industrial scale, this time is too long, so it would be advisable to find another way to shorten the mixing interval to the lowest possible time using more appropriate type of agitator, air blowing or heating. From these results the experiment was designed to eliminate the ammonia slip from coal combustion products (CCPs).

Another experiment should test the possibilities of elimination of ammonia sludge from produced solid residues after coal combustion in plants where the second method for SNCR denitrification was installed. Table 3 shows the results of the analysis of mixtures. The device's value limit is about 35 $mg \cdot l^{-1}$.

Table 3. Results of the analysis of mixtures by the ICP-OES.

	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J - L**	**M - O**
TAN [$mg \cdot l^{-1}$]	11.401	12.439	126.545	0.028	0.043	0.058	0.016	0.030	0.031	0.065	0.031
Co [$mg \cdot l^{-1}$]	37.5	35.6	*	*	*	*	*	*	*	*	*

The values of cobalt in mixture C - O were under the limit of detection. From the measured data it can be seen that the addition of the complex in the mixing water reduced the TAN content in the ash 10 times. On the other hand, the cobalt content increased to approximately 35 mg·l^{-1}. This value exceeds the determined limit by one third. However, it is clear from the results that the addition of the complex results in a significant reduction of ammonia in the water extracts. Mixtures D to I did not result in increased cobalt content in aqueous extracts after the addition of complex compound to the mixing water. The cobalt values are under the limit of detection in the case of mixtures J to K where no complex is added. The elimination is based on the formation of an insoluble ammonium complex from which the ions are no longer released into the solution.

4. Conclusion

The work was focused on the possibilities of elimination of ammonia slip from coal combustion products and from technological water. Sodium hexanitrocobaltate was added to gypsum water and to beams from mortars and pastes. It was demonstrated from the laboratory experiments that insoluble ammonium hexanitrocobaltate is released by the addition of soluble sodium hexanitrocobaltate in gypsum water. After the addition of sodium hexanitrocobaltate, total ammonium nitrogen was reduced in the samples.

The validity of this assumption was confirmed when sodium hexanitrocobaltate was added to the mixture in mixing water. If the complex compound is added to the mixing water, it is incorporated into the product volume and it does not leach into water. Which was confirmed by the aqueous extracts from mixtures, where no elevated cobalt values were measured.

Acknowledgements

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