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Release of ammonia from conventional power plant fly ash after the introduction of SNCR process

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Abstract. The paper deals with a study of various factors affecting the release of ammonia from conventional power plant fly ash after introduction of SNCR (Selective non-catalytic reduction). SNCR is a method of flue gas denitrification based on the chemical reduction of nitrogen oxide into nitrogen and water vapour. Reduction has many by-products, various ammonia salts, which could contaminate fly ash and deteriorate its properties and application. The chemical and phase composition of fly ash was determined by X-Ray Fluorescence and X-Ray Diffraction. To predict the contaminated fly ash behaviour, the samples of fly ash with known ammonia content was prepared by mixing fly ash with exact amount of ammonia hydrogensulfate. Tests were performed on the samples prepared from contaminated fly ash as it was, contaminated fly ash with deionized water and as a mixture of contaminated fly ash, lime, gypsum and water (further stabilize). Effects of various storage and mixing conditions on prepared samples properties were studied.

1. Introduction

As the main source of energy in thermal power plants is used coal. During the processes, the solid residues as fly ash and slag are produced. Coal combustion fly ash, energetic by-product, is commonly used in many branches i.e. for coal mines recultivation, terrain work or in construction industry [1].

Coal combustion produces emissions, carbon, sulfur and nitrogen oxides [2]. There are some of the processes, which can decrease the amount of emitted sulfur and nitrogen oxides. To reduce sulfur oxides emissions, the wet flue gas desulfurization is most commonly used [3]. Reduction methods as SCR (Selective catalytic reduction) and SNCR (Selective non-catalytic reduction) are the main used methods for decrease NO_x emissions. The reactions between nitrogen oxides and ammonium in the high temperature have been overall studied [4, 5]. Products of these reductions are nitrogen and water vapour. SCR process takes a place at the temperature 80–420°C and with the presence of a catalyst. SNCR process takes place at the higher temperatures, 800–900°C and without the presence of the catalyst [2]. The application of these methods in manufacturing technology could bring some technical problems. It is known, that a small amount of injected ammonia doesn't react with NO_x and results in ammonia emissions, so called ammonia slip. It typically represents less than 1% of injected ammonia, but it reacts with sulfur to form ammonium sulfate or bisulfate [6], which probable remains into a surface of fly ash or downstream equipment [7, 8, 9, 10].



Amount of ammonium salts remained on the fly ash surface depend on SO_3 content, fly ash sulfur content, an alkalinity of the fly ash, the ammonia concentration, and the ash loading in the flue gas [11].

The paper studied the properties and utilization of fly ash coming from plant where the SNCR technology is used and where the presence of unfavorable by-products is predictable.

2. Experimental

2.1. Methods

The amount of ammonia in samples was determined by a spectrophotometric method with Nessler's reagent. The first step was an extraction of ammonia to the soluble form which can be analyzed. Samples was mixed with deionized water with the ratio - 1/10 (solid/water) and the leaching procedure took place for 2 hours. Solid particles were filtered by Buchner funnel. A solution for measurement was prepared by mixing of 2.89 ml sample solution with 0.01 ml 5% solution of potassium-sodium tartrate and 0.1 ml Nessler's reagent. Absorption was measured after 10 minutes of mixing. Spectrometer HACH-LANGE DR 2800 and 1 cm cuvettes were used. The absorption wavelength was 425 nm. The concentration of ammonia was determined on the basis of the calibration primer.

2.2. Materials

Coal combustion fly ash which doesn't contain SNCR by-products (ammonia concentration lower than 5%), industrial gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), lime (CaO) and ammonium bisulfate (NH_4HSO_4) were used for preparing samples.

The chemical composition of used fly ash was examined by X-Ray fluorescence on the device Xenometric EX-6600 SSD and is given in Table 1. The phase composition of used fly ash was examined by X-Ray diffraction on the device Empyrean (Panalytical) and is given in Figure 1.

Table 1. The chemical composition of fly ash (major and minor oxides) [%].

SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	SO_3	Fe_2O_3	TiO_2	P_2O_5					
47.3	29.8	4.31	0.88	1.51	1.29	1.06	19.2	1.43	0.27					
Cr_2O_3	MnO	V_2O_5	CoO	NiO	CuO	ZnO	As_2O_3	Rb_2O_3	ZrO_2	SrO	BaO	CeO_2	Tb_4O_7	
0.02	0.18	0.07	0.02	0.02	0.03	0.07	0.08	0.02	0.03	0.04	0.10	0.04	0.02	

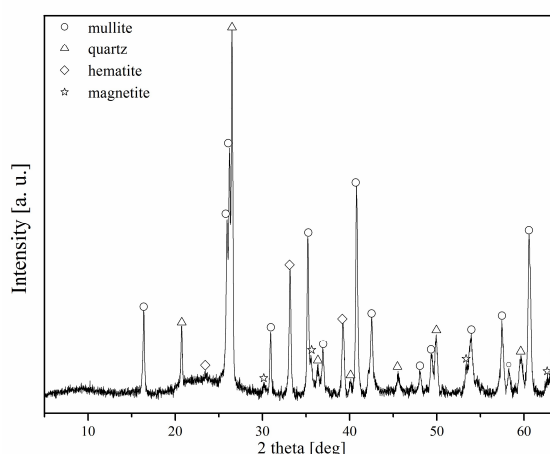


Figure 1. The phase composition of fly ash.

2.3. Tested samples

The samples were prepared from coal combustion fly ash doped by ammonium bisulfate. Fly ash, was mixed with small amount of water and ammonium bisulfate solution. The quantity of NH_4HSO_4 was chosen to correspond 50, 100, 150 and 200 ppm of NH_3 (ppm NH_3 = mg NH_3 per kg of fly ash). The wet doped fly ash was dried in a dryer at 60°C to constant weight. The real ammonia concentration of dried samples was determined by spectrophotometric method with Nessler's reagent.

In Table 2 the experiments are summarized. The three types of mixtures were tested – FA, FAW and FALG. All components (see Table 2) were put in a laboratory mixer and mixed for three minutes. Prepared samples were stored in containers without cover under the dry laboratory conditions (temperature 24°C , humidity 30%).

The effect of a mixing time and a velocity on ammonia release was examined on FAW samples. The samples were mixed for 0.5, 1, 2, 3, 5 and 10 minutes at the velocity of 58, 74, 138 and 220 rpm. The effect of the mixing time was also examined on FALG samples. First one was mixed in the laboratory mixer for 3 minutes, and then was stayed in container without cover under the dry laboratory conditions for 57 minutes. The second one was mixed for 60 minutes. The mixing velocity for both samples was 74 rpm.

The fly ash pre-heated on the temperature of 60, 80, 100 and 160°C was also used for preparing FALG samples. The fly ash was maintained at the temperature for 2 hours in the dryer and then immediately mixed with other components.

The laboratory depot simulation was performed in big container. A big container with regularly spaced small holes in the bottom was used for simulating depot in a laboratory. The container was filled with 50 kg of FAW in a layer about 40 cm. It was put in another container, where was captured water. Every 24 hours, 10 l of demineralized water was poured onto the FAW. Immediately before pouring, samples from three different levels were collected.

Table 2. Samples contain.

	FA	FAW	FALG
Fly ash [wt.%]	100	60–85	60–85
Lime [wt.%]	×	×	1-10
Industrial gypsum [wt.%]	×	×	1-10
Water [wt.%]	×	15–25	15–25

3. Results and discussion

The release of ammonia was studied on samples FA and FAW during six months. Time dependences of ammonia content are presented in Figure 2 and 3. The number of samples corresponds to the quantity of ammonia donated to fly ash by NH_4HSO_4 .

The concentration of ammonia in all samples gradually decreased with the time. After six months, the ammonia concentration was about 65% of the starting concentration. The storage of coal combustion fly ash contaminated by SNCR by-products and its using for re-cultivating purposes should have an air-polluting effect with ammonia or some ammonium compounds.

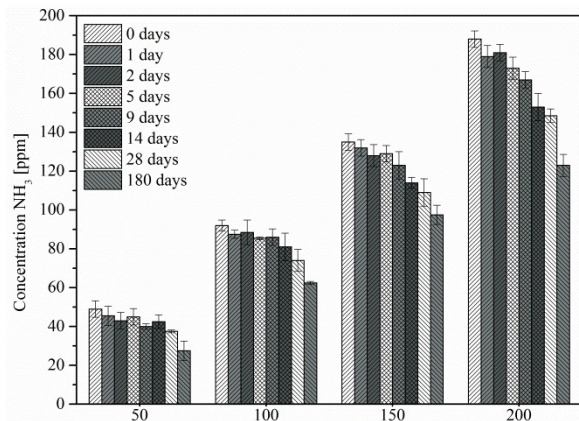


Figure 2. The time dependence of ammonia content in FA.

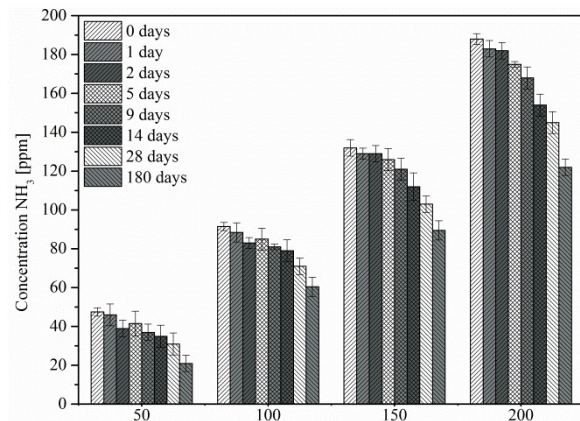


Figure 3. The time dependence of ammonia content in FAW.

The coal combustion fly ash cannot be used for storage and re-cultivation as it is, but it has to be modified. There are several different ways, how can be fly ash utilized and further used for recultivation purposes. Contaminated fly ash can be mixed with water to reduction dustiness and improve handling. This form can be used for repositories. Samples FAW simulate this way of utilization. Further samples called FALG simulate the second way of possible utilization. The way is to mix the fly ash with lime and industrial gypsum and produce a stabilized compound, which is suitable for terrain work. The process of mixing is affected by SNCR by-products. The release of ammonia during mixing process was studied and the results are presented in Figure 4 and 5.

The concentration of ammonia in samples FAW was during mixing approximately same (Figure 4) during 10 minutes. During experiments the applied mixing velocity was also studied (Figure 4) and it was observe that the increasing or decreasing velocity have not a significant effect on ammonia release. So the velocity of 74 rpm was used as optimal for experimental procedure.

Addition of lime to fly ash in aqueous conditions causes the increase of pH. Ammonium salts react in aqueous solution with high pH to create gas ammonium, which releases from the sample in very short time. Shou et al. [12] also study releases of ammonia from concrete composites. According to their results, the highest concentration of ammonia in the air above the concrete surface was after 20 minutes (around 300 ppm) from starting of mixing of batch components. They measured the concentration of ammonia in gaseous form in situ during mixing and after above the molded samples. Their results showed slightly different behavior that can be partially explained by measuring the ammonia in gaseous form instead of measuring the ammonia converted to soluble salt, as is our work. The formation of soluble salt should be affected with the high pH of used mixing solution, so the part of presented ammonia could evaporate immediately after mixing the components together. Therefore, the release measured finally in the solution could be lower.

The mixing time of FALG samples has a significant effect on the ammonia release (Figure 5). About 50% of ammonia releases in the first 60 seconds of mixing. Fast release of ammonia continues after mixing, too. Dark columns on Figure 5 presented the mixture, which was 3 minutes mixed and then stayed. The mixture could get rid of ammonia almost completely by mixing with prolonged time (Figure 5, light columns). After 60 minutes of mixing, the residual amount of ammonia was lower than 10 ppm. The resulting amount of ammonia in the mixture, which was mixed for 60 minutes, was about 15 times lower than in the mixture, which was mixed just 3 minutes.

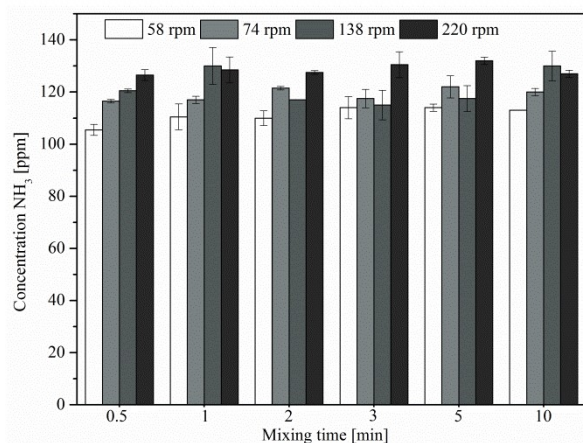


Figure 4. The mixing time dependence of ammonia content in FAW.

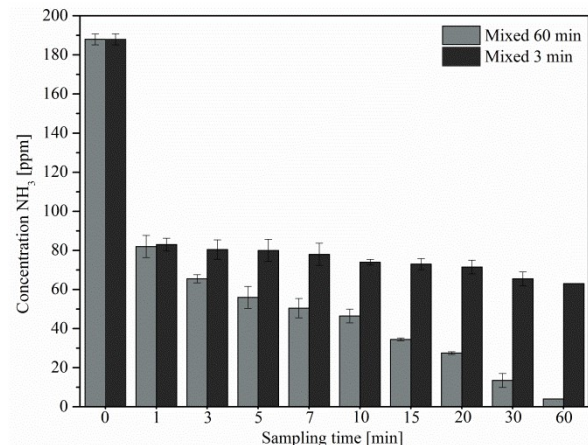


Figure 5. The mixing time dependence of ammonia content in FALG.

The fly ash is about 160°C hot when it leaves the boiler. So for the next experiment, the temperature treated fly ash was used for preparing FALG samples. The results are presented in Figure 6.

The high temperature of the fly ash slightly increases the release of ammonia. Immediately after mixing were concentrations of ammonia in samples about three times lower and after 24 hours were in all samples less than 30 ppm. It is a really low concentration which isn't healthy injurious. This ammonia concentration was reduced in next 28 days to value about 15 ppm. Maximum safe level of ammonia in the air is 25 ppm for long-term exposure (8 h) and 35 ppm for short-term exposure (15 min) [13]. So the determined values meet the requirements required for the product application.

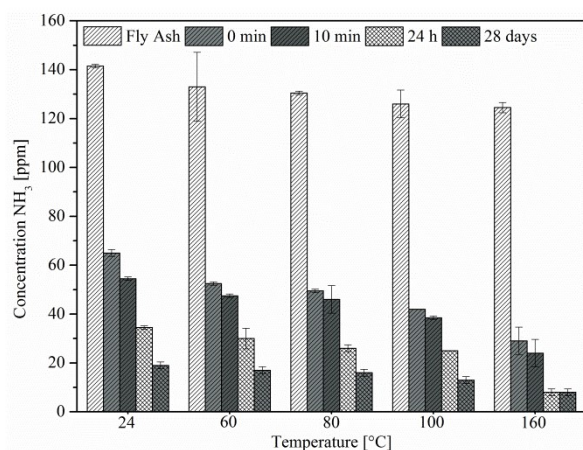


Figure 6. The temperature dependence of ammonia content in FALG.

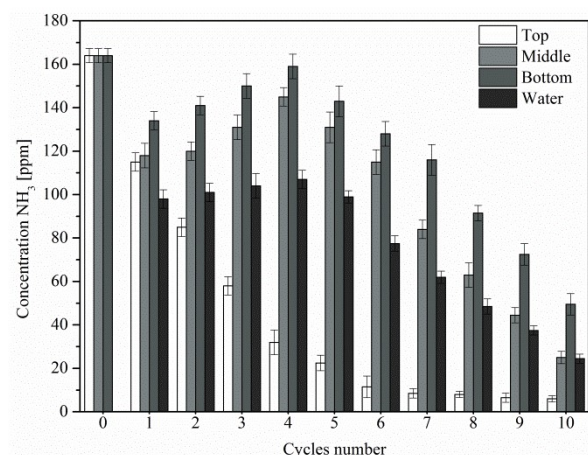


Figure 7. Depot simulation.

The results simulated the depot storage under the laboratory conditions are presented in Figure 7. Ammonium bisulfate is well soluble in water so it washes out from FAW samples. During first four cycles, the concentration in the middle and bottom decreased, because of washing out ammonium salts from the top level. The concentration of ammonia in added water, which has flowed during the FAW layer, was in the first five cycles very similar. When the concentration of ammonia in the middle and bottom level of FAW started to decrease the concentration of ammonia in flowed water decrease too. After 10 cycles, the concentration of ammonia in the top and middle levels of FAW and flowed water was lower than 30 ppm. But in the bottom level was still about 50 ppm. In the top level was less than

20 ppm of ammonia after 4 cycles. At the end of the experiment, the concentration in the top level was about 5 ppm. Similar leaching of ammonia salts studied Wang et al. in [8]. Results of their experiments confirmed, that 94% of ammonium bisulfate contained in fly ash released from mixture during first 110 minutes. This experiment show, that using coal combustion fly ash contaminated by SNCR by-products for restoring of the landscape after mining or other terrain adjustments poses a risk to the environment. The decrease of ammonia content in surface water and groundwater can have a negative impact on the life of aquatic organisms and on the quality of drinking water [14].

4. Conclusion

The presented work was focused on the release of ammonia from coal combustion fly ash contained SNCR by-products. The mentioned by-products could be various ammonium salts, most represented by ammonium sulfate and bisulfate. The salts probably aren't strongly bonded to the fly ash particles, because of ammonia content in samples storage without cover decrease with time. Such fly ash cannot be used for terrain work, because of the high solubility of ammonium salts in aqueous conditions, what has a negative impact on the environment. In the alkaline environment, ammonium releases in very short time. The mixing of samples with alkaline pH solutions has a significant effect on ammonia release. It was determined that after 60 min of mixing, the residual ammonia concentration is lower than 5% of the starting one. The high concentration of ammonia in the air has a negative impact on human health and industrial equipment. These are the reasons, why fly ash contaminated by ammonium salts cannot be used for concrete production.

Acknowledgement

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