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**ORIGINAL PAPER**

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# ASSESSMENT OF HAZARD DUE TO RELEASE OF GASEOUS AMMONIA FROM THE FLY ASH-WATER MIXTURE APPLIED IN LONGWALL MINE GOBS

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## ABSTRACT

**Purpose** The introduction of flue gas denitrification technologies by selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) in coal fired plants resulted in an increase of ammonia content in fly ash. The utilization of fly ash in fire and ventilation prevention of hard coal mines causes the release of ammonia from a fly ash-water mixture. In the applied technology of the ash and water mixture, ammonia in gaseous form is discharged and mixes with the air flowing through the mine airways. In this article, reference is made to the risk assessment of gaseous ammonia in the longwall area during the application of the fly ash-water mixture to the gobs in the U-tube ventilation system.

**Methods** The test methods include: ammonia release from ash and water mixtures at various temperatures and in respect to different proportions of water to ash with use of a multigas analyzer with an FTIR detector.

**Results** The results of the laboratory tests helped to determine the size of the ammonia stream released from the fly ash-water mixture in respect to different ratios of water to ash.

**Practical implications** Laboratory studies allow for ventilation and gaseous analysis to assess the level of ammonia risk, in the mine airways, from exhaust air discharged from the longwall area.

**Originality/value** Based on the literature review, this type of research has not been carried out so far.

**Keywords**
*ammonia, fly ash, gas hazard*

## 1. INTRODUCTION

The use of hard coal exploitation technology in hazardous conditions of spontaneous fire requires the selection of appropriate preventive measures. The most effective method for spontaneous fire risk prevention is the application of a fly ash and process water mixture, to the gobs (Krause, Łukowicz, & Piotrowski, 2009; Krause, 2009). Energy production waste has been used for many years in fire prevention in hard coal mines and has influenced both the decrease in spontaneous fire risks and the limitation of unwanted air loss through the isolation of drifts and gobs with inactive ventilation.

The ash and water mixture in hard coal mines is applied by utilizing the following technologies:

- sealing the gobs of the operated longwalls,
- sealing isolated void gobs after the operation,
- the winding-up of pits with inactive ventilation by backfilling,
- the application of long plugs insulating the closed pits and gobs from mine workings with active ventilation,
- the winding-up by backfilling of: shafts, large diameter holes, drifts, excavation chambers and other drifts.

The aforementioned mentioned technologies related to the use of the ash and water mixture in fire and gas prevention of hard coal mines are entangled with the basic activities of hard coal mining (Krause & Piotrowski, 1997; Krause, 2009).

The broad spectrum of technologies connected with the use of fly ash in coal mines leads to the reduction of air migration through gobs. Regardless of the size of the air delivery in the active drifts, the air migrates through gobs, causing minor flows despite stripping gobs by dams.

The ash and water mixture is characterized by wide usage in fire and gas prevention during drifts being wound-up by backfilling. Such winding-up procedures are usually applied at ventilation levels of mines and results from deeper excavation. Ash and water mixture applied to the liquidation of the excavation by backfilling has a significant role in reducing uncontrolled air migration through the closed pits and gobs at higher levels, and thus, reducing the risk of spontaneous fire. Air migration through gobs cause lower air delivery in active drifts of mines' ventilation system and limit air flow through gobs, and thereby reduce spontaneous fire risks. The effectiveness of the use of ash and water mixture in longwall sealing technologies is affected by many conditions, among others (Krause et al., 2009):

- the location of ash and water mixture application to the gobs,
- the fluidity of the ash and water mixture depending on the gobs slope and ratio of water to ash,
- drifts leveling on the outline of void gobs,
- the type of rocks forming direct caving in the gobs affecting the fluidity of the ash and water mixtures.

Technologies used in energetics directed at the reduction of nitrogen oxides ($NO_x$) released into the atmosphere, caused an increase in the ammonia content in the fly ash. The issues raised in the article refer to possible ammonia risks which discharges from the ash and water mixture used in underground mining.

Many factors influence the gas risks caused by ammonia release from the ash and water mixture, including the following:

- the rate of water to ash in the used mixture,
- the ash and water mixture application site ambient temperature,
- the cubage of the applied ash and water mixture per unit of time.

The Department of Environmental Monitoring of the Central Mining Institute conducted research aimed at the determination of ammonia stream size released from the ash and water mixture at varied temperatures and at deferent proportions of water to ash (Drobek, Borecki, & Bauerek, 2013).

The effectiveness of the fire prevention used, involving the sealing of longwall gobs by ash and water mixtures, determines both the adopted operation system, as well as the ventilation.

The results of the laboratory research on ammonia release from the ash and water mixture were assigned to the mixture application in the gobs ventilated by U-tube method on the body of coal. About 75% of all longwalls in Polish mines are ventilated by this method.

The fact that the ammonia releasing from the ash and water mixture during this method of ventilation migrates from the gobs to the area of the intersection of the ventilation gangway is relevant to ammonia risks. The ammonia risk assessment conducted in this article refers to the longwalls ventilated by the U-tube method on the body of coal, where the ventilation gangway in the area of the intersection with the longwall may create a risk of ammonia content exceeding the allowable limit.

## 2. LABORATORY RESEARCH ON AMMONIA RELEASE FROM THE ASH AND WATER MIXTURE

Neutralization technology of nitrogen oxides ($NO_x$) from exhaust gas in the denitrification process by the SCR or SNCR method is connected with fly ash which releases ammonia in an amount of approximately 20 ppm, i.e. 0.002 wt% $NH_3$ in 1 kg of ash, which corresponds to 26.36 $dm^3$ of pure $NH_3$ per 1000 kg of ash (Drobek et al., 2013). The method, currently being used, of SNCR denitrification guarantees a maximum ammonia content in dry energy production waste of up to 50 ppm, i.e. 65.9 $dm^3$ of pure $NH_3$ at 1000 kg ash. Given this state of affairs, it is advisable to conduct an assessment of the formation of ammonia gas hazards in excavations which are connected by the ventilation system with the areas of application of ash and water mixture.

The study of ammonia release from the ash and water mixture should take into account the temperature range of the mixture that will affect the size of the gas stream - ammonia released to the drifts into the surrounding of the workings where this process is applied (e.g., operating longwall gobs). Within the Upper Silesian Coal Basin, located in the southern part of Poland, the virgin rock temperature (VRT) as a function of depth and geothermal gradient is about one degree Celsius for each 33 meters in depth. At a depth of 25 m below the surface the VRT stands at 8°C, and as the depth increases the VRT increase is a function of geothermal gradient. At a depth of 1225 m below the surface the virgin rock temperature within the Upper Silesian Coal Basin is ca. 44°C. Taking into account the initial temperature of the rocks rising from the depth of the mine and the exploitation of a mines ultimate perspective at this depth, the research should include a temperature range of 23–45°C of the ash and water mixture.

The ratio of the ash to process water in the mixture of ash and water may vary. Depending upon the ratio of water to ash

water/solid ratio = 1 $dm^3$ of water / kg of ash = W/S

Ammonia discharge studies were performed at a ratio of water to ash in the range of 2.0–0.75. Results of the study led to the determination of the size of streams released in gaseous ammonia from the ash and water mixture, dissolved in the hydromixture aqueous phase and residual ammonia in the water drained from the mixture of ash and water (Drobek et al., 2013). The separation of these streams reduces free gas flow discharged from the ash and water mixture. The volume of ash in the mixture applied to the gobs and $NH_3$ gas volume contained in 1 Mg (megagram) dry ash enables the calculation of approximate stream of $NH_3$ released from the gobs to the excavation as a result of the application of the ash-water mixture.

The tests were performed for three ranges of temperature, which reflect changes in the ambient gobs' temperature, and hence the temperature of the mixture of the ash and water as a result of its application to gobs to the constant amount of water and variable quantities of ash supply. Tests for the six W/S ratios (Table 1) were performed in order to determine the emission of ammonia from the mixture of ash and water.

**Table 1.** Different W/S ratios of the ash-water mixture used in ammonia discharge studies

| 1 dm³ of water / kg of ash quantity | W/S |
|---|---|
| 1 dm³ water / 0.50 kg ash | 2.0 |
| 1 dm³ water / 0.57 kg ash | 1.75 |
| 1 dm³ water / 0.66 kg ash | 1.5 |
| 1 dm³ water / 0.80 kg ash | 1.25 |
| 1 dm³ water / 1.00 kg ash | 1.0 |
| 1 dm³ water / 1.33 kg ash | 0.75 |

The measurements used a closed circuit gas system with a total volume of 2000 cm$^3$, consisting of a mixer, a cooling system of the steam gas, and a computer-controlled gas analyzer with a detector operating in the infrared spectrum (FTIR) (Fig. 1).

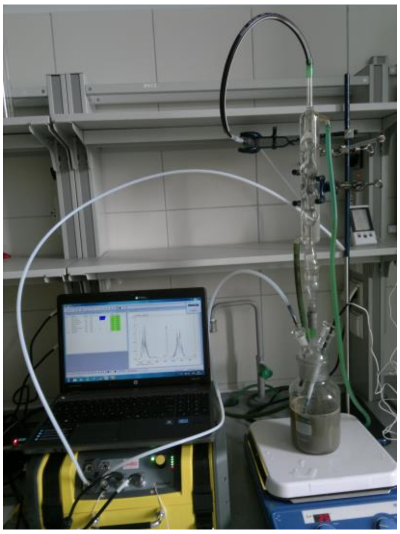

**Fig. 1.** Research reactor for the determination of the ammonia released from an ash and water mixture

Total nitrogen content and ammonia content in the samples of ash were determined before each series of ammonia release measurements. Total nitrogen content was determined by Dumas method (combustion of a sample of known mass in a high temperature, 1030°C, chamber in the presence of oxygen) with the use of an automated nitrogen analyzer where ammonia content was determined by steam distillation followed by acidimetric titration, by using a modified Kjeldahl method. The total nitrogen content consists of: nitrates (III), nitrate (V), an organic nitrogen and ammonia nitrogen. The average assay of the total nitrogen was 751 mg/kg, where ammonium nitrogen was 18.6 mg/kg, which is about 2.5% of the total nitrogen content.

For each W/S ratio an analysis of ammonia concentration in the atmosphere above the surface of the mixture of ash and water was performed. Measurements of ammonia concentration in each series of measurements were performed in the reactor every 20 seconds for at least 60 minutes.

The maximum values of ammonia content released in the production of the ash-water mixtures, depending on the W/S, is shown in Figure 2. The levels of these concentrations were reached after a minimum of 45 minutes of the experiment had been carried out.

By reducing the amount of water in the mixture of ash and water, the ammonia concentration increases in a unit volume of water, which increases the flow of $NH_3$ being discharged from the mixture. The total amount of released ammonia increases with the increase in the ambient temperature of the application area of the mixture.

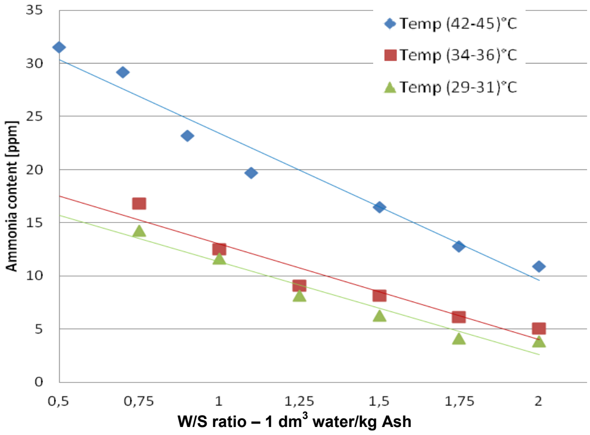

**Fig. 2.** Variation of ammonia gas release with ash-water mixture ratios at different test temperature ranges

Development of the ammonia concentration released from the mixture of ash and water in the assumed period of about 2.5 hours, in the ratio W/S of 2.0–0.75, at an operating reactor temperature of 34–36°C, is shown in Figure 3.

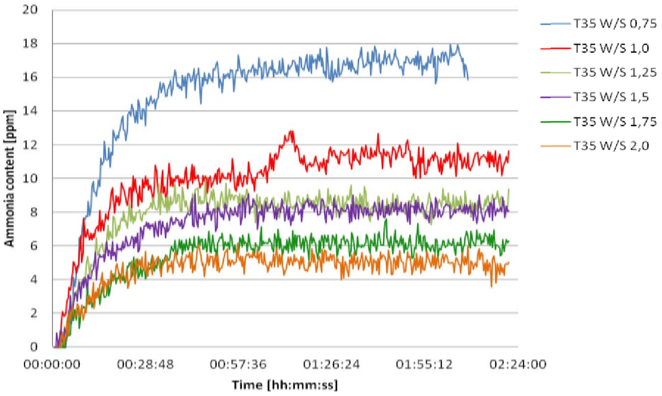

**Fig. 3.** The concentration level of ammonia discharged from the hydromixture in proportion W/S = 2.0–0.75 in the accepted time of 2.5 hours

Increasing the amount, by weight, of the ash to the same amount of water, thus reducing the W/S ratio in a mixture of ash and water, leads to a higher intensity of emission of ammonia in a short period of time.

The concentration of gaseous ammonia was marked at 11 ppm $NH_3$ at normal conditions in the range of 42–45°C temperature for the W/S ratio 2.0. A twice greater amount of ash in the hydromixture, for the W/S ratio of 1.1 at a temperature of 42–45°C, resulted in twice the ammonia emission. During the test of 2 kg of ash in 1 dm$^3$ of water (W/S 0.5) the ammonia emission to the gas phase was determined at about 30 ppm $NH_3$.

With the increase in temperature of the mixture of ash and water, ammonia release also increases. At a temperature of 29–31°C, for the W/S ratio 1.5, the concentration of gaseous ammonia was about 6 ppm $NH_3$, at a temperature of 34–36°C, 8.2 ppm of $NH_3$, while at a temperature of 42–45°C, the $NH_3$ release is 16.5 ppm, which is almost twice as much as that at a temperature range of 34–36°C.

An increase in the amount of ammonia released into the gas phase was due to the greater amount of ammonium salts dissolved in the aqueous phase hydromixture. The determined ammonia concentration in the aqueous solution after the test at a temperature of 42–45°C ranged from 3.5 mg $NH_3/dm^3$, for the W/S 2.0 mixture, to 16.4 mg $NH_3/dm^3$, for the W/S 0.5 mixture.

## 3. RISK OF GASEOUS AMMONIA IN THE LONGWALL MINING FACE VENTILATED WITH A U-TUBE VENTILATION SYSTEM

The level of the ash and water mixture, applied to the gobs, causes ammonia release in gaseous form.

The size of the stream is not without significance for the level of risk, due to the release of gaseous ammonia in the excavation area. This depends on the saturation of ash by ammonia being affected by the technology used, the volume of ash applied to the gobs in a specified time range, used the gobs' sludging and ammonia release time.

The mixture of ash and water release, aside from ammonia, gases such as: carbon dioxide, carbon monoxide, acetylene, hydrogen, ethylene, propylene, and other aromatic hydrocarbons. These gases fill the voids and migrate to the active drifts connected with the area of mixture application by a ventilation system.

A ventilation system influences the distribution of ammonia concentration from the gobs to drifts. Currently in Polish coal mines two ventilation methods dominate, i.e. the U-tube method on the body of coal and the "Y" method with the disposal of the air along the front wall.

The article analyses gas hazard resulting from gaseous ammonia in the longwalls with a U-tube method of ventilation on the body of coal. Air "leaks" of gobs $Q_{gob}$ in this ventilation method represent about 20% of the total amount of air supplied to the longwall $Q_{air}$. In terms of technology applications of the mixture of ash and water, releasing ammonia will be carried out with "leaking" air $Q_{gob}$ to the intersection area of the ventilation gangway (Fig. 4).

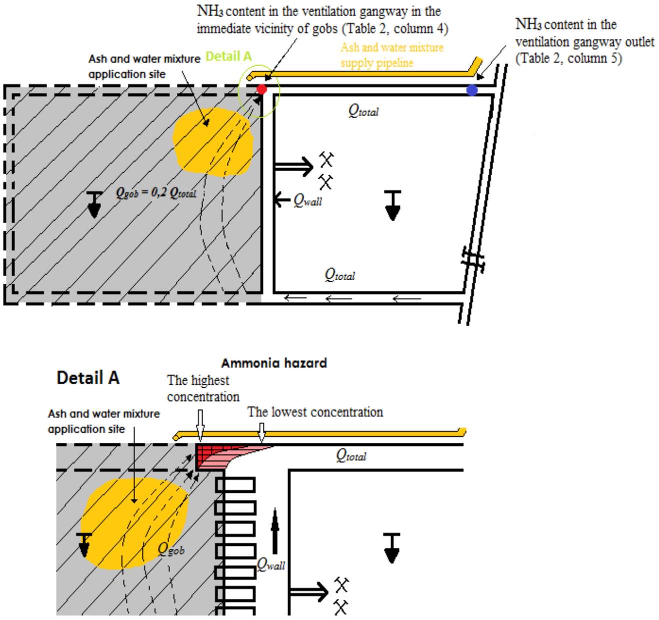

**Fig. 4.** Probable development of the ammonia threat at longwalls ventilated by a U-tube method on the body of coal

Ammonia migrating with air "leaks" to the lift could pose a threat to the crew employed on a ventilation gangway, where the U-tube method of ventilation is applied (Fig. 4).

The gas-ventilation analysis during the U-tube method of ventilation assumed air flow supplied to the wall were in the range of 300–2100 $m^3$/min. A value of 20% air migration to the gobs $Q_{gob}$ in the range of 60–420 $m^3$/min was calculated to the adopted range of air delivery to the longwall.

When applying the ash and water mixture at ratio W/S = 0.5 to gobs with ash volumes of 100 Mg, 3.16 $dm^3$ pure $NH_3$ is released. Column 4 of Table 2 shows the calculated concentration of ammonia in the immediate vicinity of gobs for the range of air supplied to the wall of 300–2100 $m^3$/min. $NH_3$ concentration at the outlet of the vent gangway was summarized in column 5 of Table 2.

**Table 2.** Calculated content of ammonia in the ventilation gangway in the immediate vicinity of gobs by the gangway outlet, for air delivered to the longwall, in the range 300 to 2100 $m^3$/min

| Air delivery $Q_{total}$ supplied to the longwall [$m^3$/min] | Air leaks through gobs 0.2 $Q_{total}$ [$m^3$/min] | Emissions of $NH_3$ from 100 Mg application of the ash and water mixture to the gobs [$dm^3$ $NH_3$/100 Mg] | The concentration of $NH_3$ in the gangway in the vicinity of gobs [ppm] | The concentration of $NH_3$ at the outlet of the vent gangway [ppm] |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| 300 | 60 | 3.16 | 52 | 10.5 |
| 500 | 100 | | 31.6 | 6.3 |
| 700 | 140 | | 22.5 | 4.5 |
| 900 | 180 | | 17.5 | 3.5 |
| 1100 | 220 | | 14.4 | 2.9 |
| 1300 | 260 | | 12.1 | 2.4 |
| 1500 | 300 | | 10.5 | 2.1 |
| 1700 | 340 | | 9.2 | 1.8 |
| 1900 | 380 | | 8.3 | 1.6 |
| 2100 | 420 | | 7.5 | 0.7 |

The irritant effect on the value of the maximum allowable concentration (MAC) of ammonia, as a weighted average for an 8-hour working day, is 14 $mg/m^3$ (19.74 ppm), and the value of the maximum permissible instantaneous concentration, defined as exposure of no more than 15 minutes and not more than 2 times during a working shift with intervals of not less than 1 hour, is 28 $mg/m^3$ (39.48 ppm) (Rozporządzenie, 2002).

Listed values in columns 4 and 5 of the calculated concentrations of $NH_3$ confirm that the application of the ash and water mixture to the gobs, ventilated by the U-tube method, may cause exceeded levels of ammonia in excavations in the immediate vicinity of gobs.

## 4. CONCLUSION

The results of laboratory research of ammonia discharge from the ash and water mixture and the ventilation and gas analysis of gaseous ammonia from mixtures of ash and water to the walls ventilated using the U-tube method on the body of coal, allow us to present the following conclusion:

- mining technologies using fly ash, created in $NO_x$ reduction systems, can cause gas hazards by gaseous ammonia release into the ventilation air of mine drifts,
- gas hazards may occur as a result of ammonia release to mine air from the mixture of ash and water used in applied technologies, which result in exceeding the permissible concentrations,
- ammonia gas hazards may occur at ventilation gangways with the U-tube ventilation method on the body of coal, mainly in the vicinity of gobs behind the longwall face,
- the distribution of ammonia concentration in the immediate vicinity of gobs at ventilation gangways with the U-tube ventilation method may lead to the levels of ammonia in the air exceeding permitted levels,
- ammonia content at the outlet of ventilation gangways will not exceed the limit values regulations, regardless of the ventilation method.

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