

Experimental model of ammonia elimination by ozone in the air

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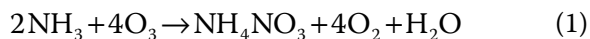
Abstract

HUTLA P., PETRÁČKOVÁ B., KÁRA J., 2013. **Experimental model of ammonia elimination by ozone in the air**. Res. Agr. Eng., 59: 39–45.

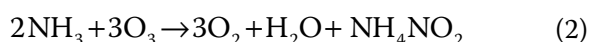
Experimental device was created to model stable atmosphere. The device consists of the glass vessel filled with air. Volume of the vessel is 30 litres. The ammonia concentration is similar to stable air. Amount of ozone in 2.4 mg was added and subsequently weight loss of ammonia was measured. Measurements were performed at different temperatures (20°C, 45°C) and different air humidity. The observed ratio of reacting ozone and ammonia is 5.2:1. It was also found, that this ratio is practically independent of temperature and relative humidity that occur in a stable environment. The results are the basis for the design of ozone air purification technology.

Keywords: stable atmosphere; air purification technology; animal stables; air purification by ozone

The impact of ozone on the reduction of the ammonia concentration in the air was tested in order to determine the amount of ozone necessary in the environment of animal stables. The fundamental mechanism of the ozonizing process with the goal of reducing the concentration of the ammonia in the air assumes powerful oxidation qualities of ozone which through a chemical reaction reduces the ammonia. The reaction between ozone and ammonia was periodically investigated in the past 90 years. It can be simply described as (Wikipedia 2010):



Aside from Eq. (1), older studies present another possible reaction (STRECKER, THIENEMAN 1920):



In the study, an observation was made that during a certain period of time the ozone bubbles

through the ammonia solution; at the temperature -78°C the solution assumes an intense red-orange colour. With an increased temperature, the colour fades and disappears at -60°C . Red-orange compound was analysed in several studies. It was identified (SOLOMON et al. 1962) as ammonia ozonide $\text{NH}_4^+\text{O}_3^-$.

The reaction kinetics $\text{NH}_3\text{-O}_3$ producing NH_4NO_3 were studied in a water solution (HOIGNÉ, BADER 1978) in the gas stage (OLSZYNA, HEICKLEN 1972) as well as in the condensation stage (HUSTON et al. 1983). If ozone and ammonia react in the gas stage at room temperature, the majority of the products are NH_4NO_3 , O_2 and H_2O , produced according to the noted Eq. (1). This was documented by findings that the amount of produced gas products relative to the reacting ozone is 1.05 (O_2) and 0.31 (H_2O) (OLSZYNA, HEICKLEN 1972). Compare to these stated chemical mechanics, it is noted that the ozone reaction to multiple inner air contaminants

can be active for several months (BOENIGER 1995). It is also noted, that a direct oxidation of ammonia through the ozone in the water solution is fairly slow (HOIGNE 1998).

What is important for further applications in practice is that the half-life of the ozone disintegration lasts from 2.5 to 7 min, however in a clean environment this value can increase to 60 min (KEENER et al. 1999). In other sources (Wikipedia 2010), the half-life of ozone disintegration is stated as 45 min at 20°C and 20 min at 30°C. The ozone concentration is being reduced according to the following equation:

$$\rho = \rho_0 \times 2^{-t/t_h} \quad (3)$$

where:

ρ – ozone concentration (g/m³)

ρ_0 – concentration at the beginning (g/m³)

t_h – half-life of disintegration (min)

t – time (min)

While applying the Eq. (1), the following are the resulting ratios of the entering and exiting compounds (NH₃:O₃:NH₄NO₃:O₂:H₂O): 34:192:80:128:18.

MATERIAL AND METHODS

A series of lab work was done in order to demonstrate the applications in practice. Amounts of ozone and ammonia entering their reaction were sampled in order to determine how much ozone is necessary to add in order to eliminate a given amount of ammonia from the air. A tightened glass container of 30 l capacity was used for the experiments. Diagnostic equipment Data logger NH₃ (Protronix, Chrudim, Czech Republic) (Fig. 1) was used to determine concentration of the ammonia. This diagnostic apparatus allows for an independent recording of NH₃ values, temperature and relative humidity of the air during one minute, range of diagnosing the NH₃ concentration is 0–50 ± 2 ppm; temperature is measured in the range between 0 and 40 ± 0.5°C, air humidity 0–100% (up to 90 ± 2 %). The apparatus can be connected through a USB cable to a computer which allows for a direct reading of the specific quantities. For the purpose of homogenization with a possible warm-up of the air in the container, an apparatus was constructed to include a ventilator with a diameter of 45 mm and a series of halogen lights with input 3 × 50 W. The entire equipment was powered by a source of voltage 12 V. The



Fig. 1. Data logger NH₃

entry points of the power and measuring conductors were inserted and fully sealed into the lid of the container. The lid also contained closable openings for the entry and exit of gases. The entire measuring system for confirmation of reaction O₃ and NH₃ is shown in the Fig. 2.

A portable ozone generator (Fig. 3), brand ITTU 500.ACE (AZCO Industries, Langley, Canada), is the source of the actual ozone. The principle of this equipment is based on the electrical discharge (corona discharge), during which the two-atom oxygen molecules divide themselves into singular atoms, which then re-connect, partially into three-atom molecules. The entering air is being dried us-



Fig. 2. Measuring equipment for confirmation of reaction O₃-NH₃



Fig. 3. Portable ozone generator ITTU 500.ACE

ing silica-gel heaters/dryers to practically a zero value of relative humidity. The ozone generator allows for regulation of the entering volume of air as well as the intensity of the source of the ozone.

For further confirmation of the reaction between $\text{NH}_3\text{-O}_3$, the density values of the ammonia and ozone were found to be of importance at various temperature levels, as well as the resulting volume and mass concentrations.

In case of ammonia:

$$\rho = 0.73 \text{ kg/m}^3 \quad \text{at } 15^\circ\text{C}$$

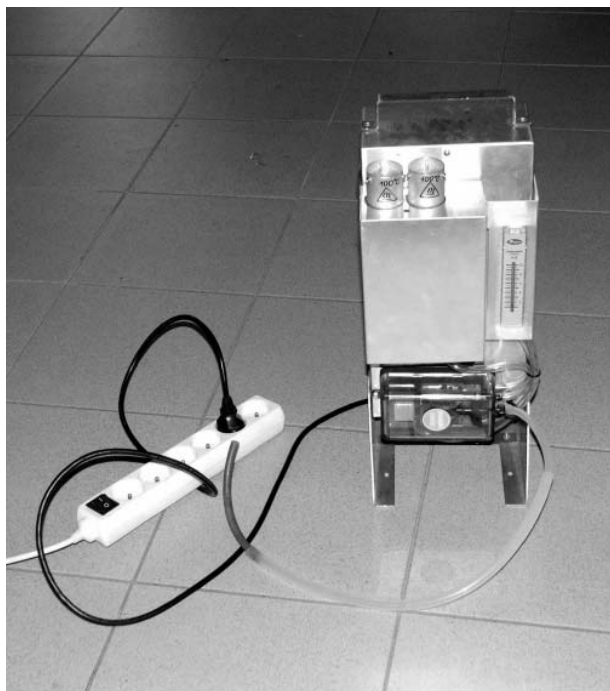


Fig. 4. Ozone measuring equipment APOA 350 E in the diagnostic vehicle

In case of ozone:

$$\rho = 2.144 \text{ kg/m}^3 \quad \text{at } 0^\circ\text{C}$$

For calculations of the density value at different temperature levels, the following equation may be used:

$$\frac{V}{T} = \text{const.} \quad (4)$$

where:

V – volume of the gas (m^3)

T – the absolute temperature of the gas (K)

and which means $\rho \times T = \text{const.}$

where:

ρ – the density of the gas (kg/m^3)

During the measurements, the reached ammonia concentration was up to 70 ppm, which corresponded to the amount of approximately up to 1.7 mg. According to the Eq. (1) in order to create reaction of this amount of ammonia, about 9.5 mg of ozone was necessary. This corresponds to the amount of 6 l at the exiting ozone concentration of 1.6 g/m^3 . Prior to the beginning of each reaction, the container was rinsed with the technical air, which among other also achieved a very low level of relative humidity of the gas.

Confirmation of calibration dependence of the ozone generator. Since the quantities of the reacting gases are being confirmed in the container, it is necessary to assure for sufficient exactness of the found mass of the reacting ozone. For this purpose, the ozone concentration level at the exit from the ozone generator was determined by using the measuring equipment APOA 350 E (Horiba, Kyo-

Table 1. Reaction $\text{NH}_3\text{-O}_3$ in the air with low relative humidity of gas in the vessel with a capacity of 30 l

Beginning			Finally			NH ₃ density (kg/m ³)	Change of NH ₃		
NH ₃ concentration (ppm)	temperature (°C)	relative humidity (%)	NH ₃ concentration (ppm)	temperature (°C)	relative humidity (%)		concentration		mass
							(ppm)	(mg/m ³)	(mg)
28.7	19.5	5.3	8.3	19.9	11.1	0.72	20.4	14.7	0.44
65.8	20.1	1.4	44.7	20.4	6.2	0.72	21.1	15.2	0.46
61.5	20.9	5.1	40.7	21.3	10.2	0.72	20.8	15.0	0.45
34.5	20.8	6.1	12.8	21.2	11.8	0.72	21.7	15.6	0.47
42.8	19.8	2.6	20.0	20.8	7.2	0.72	22.8	16.4	0.49
40.3	21.1	3.4	17.2	22.0	8.1	0.72	23.1	16.6	0.50
31.2	20.2	4.3	10.5	20.9	9.7	0.72	20.7	14.9	0.45
38.1	20.3	2.7	17.6	20.9	8.1	0.72	20.5	14.8	0.44
41.7	19.7	2.3	20.5	20.6	8.7	0.72	21.2	15.3	0.46
50.8	19.6	3.2	28.5	20.3	9.2	0.72	22.3	16.1	0.48
53.6	21.2	5.1	32.9	21.8	11.7	0.72	20.7	14.9	0.45
58.1	20.8	1.2	37.3	21.6	7.2	0.72	20.8	15.0	0.45
36.5	20.8	2.7	14.1	21.7	8.1	0.72	22.4	16.1	0.48
40.0	20.7	5.7	19.0	21.7	10.1	0.72	21.0	15.1	0.45
51.8	21.0	3.2	30.7	21.5	7.9	0.72	21.1	15.2	0.46
32.1	19.9	4.6	10.5	20.5	9.9	0.72	21.6	15.6	0.47
35.7	21.2	4.6	13.6	21.8	10.3	0.72	22.1	15.9	0.48
43.6	19.7	3.1	21.9	20.4	9.1	0.72	21.7	15.6	0.47
25.6	21.3	2.1	4.7	21.7	8.2	0.72	20.9	15.0	0.45
32.1	20.8	1.8	10.3	21.6	7.9	0.72	21.8	15.7	0.47
40.8	43	6	15.9	43	6.8	0.67	24.9	16.7	0.50
34.5	45	3.3	11.8	45	4.6	0.66	22.7	15.0	0.45
23.8	46	4.2	0.6	46	5.1	0.66	23.2	15.3	0.46
50.1	46	5.1	28.2	46	6.0	0.66	21.9	14.5	0.43
66.0	45	6.0	37.8	45	6.5	0.66	28.2	18.6	0.55
42.8	46	6.2	18.6	46	6.8	0.66	24.2	16.0	0.48
38.1	45	3.8	15.9	46	4.7	0.66	22.2	14.7	0.44
45.7	45	4.2	21.5	45	5.0	0.66	24.2	16.0	0.48
49.7	46	5.1	26.0	46	5.9	0.66	23.7	15.7	0.47
37.2	44	4.1	14.4	45	5.2	0.66	22.8	15.1	0.45
52.8	46	4.8	28.6	46	5.7	0.66	24.2	16.0	0.48
50.0	43	3.1	25.1	44	4.0	0.67	24.9	16.7	0.50
41.1	44	5.1	19.2	45	5.9	0.66	21.9	14.5	0.43
28.3	45	5.7	6.1	46	6.6	0.66	22.2	14.7	0.44
27.7	44	4.6	4.9	45	5.5	0.66	22.8	15.1	0.45
32.3	46	4.2	8.6	46	5.0	0.66	23.7	15.7	0.47
37.1	44	3.1	14.9	44	4.1	0.66	22.2	14.7	0.44
29.9	45	4.3	6.7	46	5.2	0.66	23.2	15.3	0.46
42.3	46	3.1	18.6	46	4.0	0.66	23.7	15.7	0.47
40.0	44	4.2	17.8	45	5.0	0.66	22.2	14.7	0.44

Table 2. Reaction $\text{NH}_3\text{-O}_3$ in the air with high relative humidity of gas in the vessel with a capacity of 30 l

Beginning			Finally			NH ₃ density (kg/m ³)	Change of NH ₃		
NH ₃ concentration (ppm)	tempera- ture (°C)	relative humidity (%)	NH ₃ concentration (ppm)	tempera- ture (°C)	relative humidity (%)		concentration		mass
							(ppm)	(mg/m ³)	(mg)
60.5	20.9	49	33.5	21.0	49	0.72	27.0	19.4	0.58
33.5	21	49	13.8	21.1	49.1	0.72	19.7	14.2	0.43
46.9	21.2	50.2	26.2	21.2	50.4	0.72	20.7	14.9	0.45
51.3	21.5	49.8	29.7	21.7	49.8	0.71	21.6	15.3	0.46
50.0	21.4	49.7	27.9	21.4	49.9	0.71	22.1	15.7	0.47
31.4	20.8	49.9	11.0	20.9	49.9	0.72	20.4	14.7	0.44
42.3	21.7	49.2	19.8	21.9	49.5	0.71	22.5	16.0	0.48
42.7	20.8	49.7	22.3	20.9	50.0	0.72	20.4	14.7	0.44
49.9	21.2	49.2	30.2	21.2	49.2	0.72	19.7	14.2	0.43
29.3	21.3	49.3	8.6	21.4	49.4	0.72	20.7	14.9	0.45
32.8	21.2	49.8	10.6	21.2	49.9	0.72	22.2	16.0	0.48
41.0	21.0	50.1	20.6	21.3	50.2	0.72	20.4	14.7	0.44
32.4	20.9	50.2	11.7	21.2	50.3	0.72	20.7	14.9	0.45
38.8	21.3	50.2	18.4	21.4	50.2	0.72	20.4	14.7	0.44
46.3	21.2	49.2	24.5	21.2	49.3	0.72	21.8	15.7	0.47
47.1	21.0	49.7	25.8	21.0	49.9	0.72	21.3	15.3	0.46
36.2	20.9	49.5	15.8	21.1	49.7	0.72	20.4	14.7	0.44
31.3	21.3	50.0	8.6	21.3	50.1	0.72	22.7	16.3	0.49
40.1	21.2	49.8	16.5	21.5	49.8	0.72	23.6	17.0	0.51
36.6	21.2	49.7	16.2	21.1	49.6	0.72	20.4	14.7	0.44
29.7	21.5	80.1	7.4	21.5	78.5	0.71	22.3	15.8	0.47
31.9	21.6	80.0	9.8	21.6	78.6	0.71	22.1	15.7	0.47
48.2	21.2	80.1	27.8	21.3	78.6	0.72	20.4	14.7	0.44
41.9	21.1	79.8	21.1	21.2	78.3	0.72	20.8	15.0	0.45
47.1	20.9	79.9	26.7	20.9	78.4	0.72	20.4	14.7	0.44
32.8	21.4	80.0	10.3	21.5	78.5	0.71	22.5	16.0	0.48
37.1	21.7	80.2	14.1	21.7	78.8	0.71	23.0	16.3	0.49
32.4	21.5	80.0	12.7	21.6	78.9	0.71	19.7	14.0	0.42
37.7	21.6	79.7	17.0	21.7	78.4	0.71	20.7	14.7	0.44
47.2	21.7	79.8	25.1	21.7	78.2	0.71	22.1	15.7	0.47
41.8	21.9	80.2	18.3	21.9	78.2	0.71	23.5	16.7	0.50
29.5	21.2	79.1	7.7	21.3	77.8	0.72	21.8	15.7	0.47
34.4	21.2	79.7	10.3	21.5	78.1	0.72	24.1	17.3	0.52
44.5	20.9	79.6	22.7	20.8	78.5	0.72	21.8	15.7	0.47
47.1	21.5	79.9	26.4	21.7	78.4	0.71	20.7	14.7	0.44
38.1	21.2	80.0	16.8	21.4	78.7	0.72	21.3	15.3	0.46
31.9	21.7	80.1	13.2	21.7	78.4	0.71	19.7	14.0	0.42
37.7	21.6	79.9	15.2	21.7	78.5	0.71	22.5	16.0	0.48
40.1	21.7	80.0	17.1	21.7	78.9	0.71	23.0	16.3	0.49
32.8	21.2	80.1	12.4	21.4	78.4	0.72	20.4	14.7	0.44

to, Japan). The measuring equipment (Fig. 4) is a part of a diagnostic vehicle, which is being administered by the State Medical Institute, Prague. The measuring equipment operates on the principle of UV light absorption, supported by the Cross-Flow modulation technique. This technique minimizes any possible fluctuation of the zero, it assures the long-term stability of the measurements and allows the measurement to be highly sensitive. The technician uses the heated container to produce the referenced gas by the decomposition of the O_3 in the sample. This causes some limited interference as well as a higher resistance against the presence of humidity in the sample. The range of the measurements is 0–100/200/500/1000 ppb (e.g. approximately up to 2 mg/m^3). The reproducibility of the measurements is 1% of the full deviation, threshold of detection is 0.3 ppb.

The process of the measurements was as follows. A tedlar bag of volume 47 l was filled with technical air. 1 ml of ozone-rich air from the ozone generator was added. The ozone generator was set to produce ozone in the intensity No. 10 with the flow amount of 1.5 l/minute. Once set, the air was let go into the measuring equipment Horiba. The confirmed ozone concentration was in the range of 33 to $35 \text{ } \mu\text{g/m}^3$. Out of that, the calculated ozone concentration in the exit area of the ozone generator with 1.6 g/m^3 , plus minus 5%. This process was repeated three times with the same results. Next, the amount of added ozone air was increased to 3 ml. The resulting concentration in the bag was determined to be 103 to $106 \text{ } \mu\text{g/m}^3$.

RESULTS AND DISCUSSION

The results of the reduction of concentration of ammonia by adding ozone (as measured at various temperature levels of gas), are shown at Table 1. In all cases, dry ozone-rich air was being added with ozone concentration of 1.6 g/m^3 during one minute, e.g. total of 2.4 mg of ozone. Table 1 shows the amount of ammonia reacting with 2.4 mg of ozone. The confirmed amounts are in the range of 0.43 to 0.55 mg; mid value with temperature level of $21 \pm 1^\circ\text{C}$ is 0.46 mg with standard deviation of 0.016 mg. For temperature level of $44.5 \pm 1.5^\circ\text{C}$ then 0.46 mg with standard deviation 0.028 mg. In comparison with the Eq. (1) it is clear that the ratio $O_3:NH_3$ here is lower – 5.2:1. However, for practical applications, it is relatively satisfactory.

Next, the influence of relative humidity of the gas on the mass ratio of O_3 and NH_3 during the reaction was being investigated. The results are shown in Table 2. The amount of ammonia, which reacts with 2.4 mg of ozone is according to Table 2 similar as during the reaction in the environment with a very low relative humidity (Table 1). The confirmed amounts are in the range of 0.42 to 0.58 mg, the mean value for relative humidity of 50% being 0.46 mg with standard deviation of 0.034 mg, for relative humidity of 80% being 0.46 with standard deviation of 0.026 mg. Ratio $O_3:NH_3$ being again 5.2:1.

CONCLUSIONS

The measurements confirmed the mass ratios in the reaction of O_3 and NH_3 within the gas environment. The ratio of the reacting materials is 5.2:1. A possibility of an error in this ratio depends on the exactness of the measurements of the reacting ammonia, e.g. with the maximum of the standard deviation, as well as an error in the measurements of the amount of the ozone, which depends on the exactness of the measuring apparatus and the error of the measurements itself, total of 10%. The entire possible error in determining the mass ratios is therefore under 15%.

Ammonia is the most important gas pollutant in livestock buildings. Its elimination or possible significant reduction of its concentration by ozone technologies is one of the perspective trends of technical development. The result is either a direct improvement of stable environment, or reduction of negative impact of animal production on the living environment. Knowledge of the required amount of added ozone is the necessary assumption for design and project of ozonizing device. When using ozone technology, it is possible to install the source of ozone into the entire of air-conditioning system. In this case, ozone works for improvement of the quality of air in the area of animal husbandry. Here, it is necessary to watch carefully the permitted limits of O_3 throughout the interior. In the simple case, the sources of ozone can be installed in the outlet pipe of the air conditioning system. It leads to the elimination of ammonia emissions into the surrounding area.

The experimental stage confirmed a satisfactory agreement with the theoretical assumptions and the confirmed quantity ratios may be used for practical applications of ozone technology in the animal

stable environment. It was also confirmed especially for the practical working applications, that the mass ratios of the particles of O_3 and NH_3 are not dependent during this reaction on the relative humidity either on the air temperature of the gas, in which this reaction proceeds.

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Received for publication July 9, 2012

Accepted after corrections September 3, 2012

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