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NEW DEVELOPMENTS IN METHANE FERMENTATION AND AMMONIA EMISSION TO OBTAIN BETTER ENVIRONMENTAL CONDITIONS FOR LIVING IN COUNTRY SIDE AREA

NOWE ROZWIĄZANIA W FERMENTACJI METANOWEJ I EMISJI AMONIAKU W CELU UZYSKANIA LEPSZYCH WARUNKÓW ŚRODOWISKOWYCH DO ŻYCIA NA OBSZARACH WIEJSKICH

***Summary**: Research results indicate the growing ammonia concentration in the air and the necessity to undertake the work aimed at the change of the mentioned situation, using different solutions. University of Maryland (USA) undertook the study of global ammonia concentrations in the air over the most productive agricultural regions in the world. Acidification of animal slurry has proved to be an efficient solution to minimize NH_3 emissions in-house, during storage, and after soil application, as well as to increase the fertilizer value of slurry, without negative impacts on other gaseous emissions. This solution has been used commonly in Denmark, and its efficiency with regard to the minimization of NH_3 emissions has been documented in some studies. Slurry acidification technology gives many advantages from the point of view of soil fertilization and also the limiting of ammonia emission. Acidification reduced NH_3 emission from the stored slurry to less than 10% of the emission from untreated slurry, and the NH_3 emission from the slurry employed on the field was reduced by 67%. Of course it requires providing the safety procedures to avoid a direct contact of farm workers with harmful activity of the acid. Reducing the loss of nitrogen from agriculture has a key meaning for reduction of eutrophication of the Baltic Sea. Most of the airborne eutrophication to the Baltic Sea comes from the ammonia emissions, and in the BSR almost all ammonia emissions come from livestock manure. Annual deposition of ammonia nitrogen to the Baltic Sea has been increasing during the recent years and was greater in 2012 than in 1995. While emissions are decreasing slightly in some countries, HELCOM Baltic Sea Action Plan calls for a reduction of 118.000 tonnes of nitrogen annually to the Baltic Sea, and the Revised Gothenburg Protocol (2012) calls for ambitious reductions in ammonia emissions from all BSR countries. Slurry acidification also affects solid/liquid slurry separation efficiency positively; DM is higher, N lower and P higher in the solid fraction. A combined treatment should efficiently prevent gaseous emissions, increase fertilizer value of slurry and reduce transport and energy costs. The pH level of 5.5- 6.4 is not very acidic, and no more acidic than rain water, which has a normal pH range from 4.5 to 8.5. Biogas experiments show the possibility of utilization of slurry with high dry matter content in biogas production.*

***Keywords**: new technology, slurry acidification technology, ammonia emission, environment protection, biogas production*

***Streszczenie**: Wyniki badań wskazują na rosnące stężenie amoniaku w powietrzu i konieczność podjęcia pracy nad zmianą tej sytuacji przy zastosowaniu różnych rozwiązań. University of Maryland (USA) podjął się badania globalnych stężeń amoniaku w powietrzu nad najbardziej produktywnymi regionami rolniczymi na świecie. Zakwaszanie gnojowicy zwierzęcej okazało się skutecznym rozwiązaniem minimalizującym emisję NH_3 w gospodarstwie, podczas przechowywania i po zastosowaniu doglebowym, a także zwiększającym wartość nawozową gnojowicy bez negatywnego wpływu na inne emisje gazowe. Rozwiązanie to jest powszechnie stosowane w Danii, a jego skuteczność w zakresie minimalizacji emisji NH_3 została udokumentowana w niektórych badaniach. Technologia zakwaszania gnojowicy daje wiele korzyści z punktu widzenia nawożenia gleby, a także ograniczenia emisji amoniaku. Zakwaszenie ograniczyło emisję NH_3 z magazynowanej gnojowicy do mniej niż 10% emisji z gnojowicy nieoczyszczonej, a emisja NH_3 z gnojowicy stosowanej na polu została zmniejszona o 67%. Oczywiście wymaga to zapewnienia procedur bezpieczeństwa, aby uniknąć bezpośredniego kontaktu pracowników rolnych ze szkodliwym działaniem kwasu. Ograniczenie strat azotu z rolnictwa ma kluczowe znaczenie dla ograniczenia eutrofizacji Morza Bałtyckiego. Większość eutrofizacji przenoszonej drogą powietrzną do Morza Bałtyckiego pochodzi z emisji amoniaku, a w BSR prawie wszystkie emisje amoniaku pochodzą z obornika zwierzęcego. Roczna depozycja azotu amonowego w Morzu Bałtyckim wzrastała w ostatnich latach i była większa w 2012 r. niż w 1995 r. Podczas gdy emisje w niektórych krajach nieznacznie spadają, Bałtycki Plan Działania HELCOM zakłada redukcję o 118 000 ton azotu rocznie do Morza Bałtyckiego oraz zrewidowany protokół z Göteborga (2012) wzywa do ambitnych redukcji emisji amoniaku ze wszystkich krajów BSR. Zakwaszenie gnojowicy wpływa również pozytywnie na skuteczność separacji gnojowicy ciało stałe/ciecz; DM jest wyższy, N niższy, a P wyższy we frakcji stałej. Połączona obróbka powinna skutecznie zapobiegać emisjom gazów, zwiększać wartość nawozową gnojowicy oraz obniżać koszty transportu i energii. Poziom pH 5,5-6,4 nie jest bardzo kwaśny i nie bardziej kwaśny niż woda deszczowa, która ma normalny zakres pH od 4,5 do 8,5. Doświadczenia biogazowe wskazują na możliwość wykorzystania gnojowicy o wysokiej zawartości suchej masy do produkcji biogazu.*

***Słowa kluczowe**: nowa technologia, technologia zakwaszania gnojowicy, emisja amoniaku, ochrona środowiska, produkcja biogazu*

Introduction

Ammonia in the gaseous state is a natural part of the nitrogen cycle in nature, but excessive concentration harms plants and lowers water and air quality. In the lowest atmosphere, the troposphere, ammonia reacts with nitric and sulfuric acids to form nitric-containing particles, adding to the air pollution. Researchers from University of Maryland (USA) undertook the first long-term study of global ammonia concentrations in the air over the four most productive agricultural regions in the world.

They used data from NASA's Atmospheric Infrared Sounder (AIRS) satellite. Their analysis shows that between 2002 and 2016, ammonia concentrations over agricultural regions in the USA, Europe, China and India continued to grow. This, in turn, translates into ever-deeper water and air quality in these areas. Despite the differences between the different areas, the main factors influencing the increase in ammonia are according to researchers: the use of fertilizers, slurry matter of farm animals, changes in the composition of the atmosphere and warming of the soil, which retain less ammonia. The study was published in March 2017 in "Geophysical Research Letters". Ammonia can also sink back into the ground and into lakes, rivers and oceans, where it contributes to the flowering of harmful algae and the formation of so-called dead zones with a very low oxygen content. Taking into account four studied regions of the world, the smallest increase in ammonia concentrations in the air was recorded in Europe. According to the researchers, we are partially owing to the regulations limiting the use of ammonia fertilizers and there are better methods of livestock waste disposal. However, the main factor was probably - as in the United States - the reduction of the so-called acid rain which previously removed ammonia from the atmosphere. Slurry acidification can be explained as equilibrium between the water bound ammonium (NH_{4+}) and the volatile ammonia (NH_3) is moved towards ammonium by adding acid to the slurry. Normally, concentrated sulfuric acid is used, and the costs of the acid in many cases outweighed by savings on purchase of S fertiliser. The nitrogen that is captured via avoided ammonia evaporation is turned into savings on purchase of N fertiliser, or in higher crop yields. Slurry acidification also has a considerable climate effect by increasing the carbon sequestration in soil. Reducing the loss of nitrogen from agriculture is crucial to reducing eutrophication of the Baltic Sea. Most of the airborne eutrophication to the Baltic Sea comes from ammonia emissions, and in the BSR almost all ammonia emissions are from livestock manure. Annual deposition of ammonia nitrogen to the Baltic Sea has been increasing during the recent years and was greater in 2012 than in 1995. While emissions are decreasing slightly in some countries, HELCOM Baltic Sea Action Plan calls for a reduction of 118.000 tonnes of nitrogen annually to the Baltic Sea, and the Revised Gothenburg Protocol (2012) calls for ambitious reductions in ammonia emissions from all BSR countries. Slurry acidification also affects solid/liquid slurry separation efficiency positively; DM is higher, N lower and P higher in the solid fraction. A combined treatment should efficiently prevent gaseous emissions, increase fertilizer value of slurry and reduce transport and energy costs.

Development of slurry acidification technology

Technical report concerning feasibility studies for pilot installations of Interreg SAT's activity was provided by Institute of Technology and Life Sciences in Falenty Branch in Warsaw. In application form "in storage" system was planned to be utilized in Polish conditions. In the project there are involved all Baltic countries: Sweden, Denmark, Finland, Germany, Poland, Estonia, Lithuania and Latvia. Also, Russia and Belarus are involved as cooperating members of the project. ITP has three experimental farms located at a distance of about 300 km one from the other. In each of them, there were the farms having the barns with approximately about 180 cows in each site. Experimental farm in Falenty has chemical laboratory, which can provide sample tests taken from acidification experiments. This situation made a decision to plan two concrete tanks of approximately 12.5 m^3 each to provide two different experiments: slurry acidification research and concrete tests concerning influence of harmful substances on the construction material itself. Acidification of animal slurry has proved to be an efficient solution to minimize NH_3 emissions in-house, during storage, and after soil

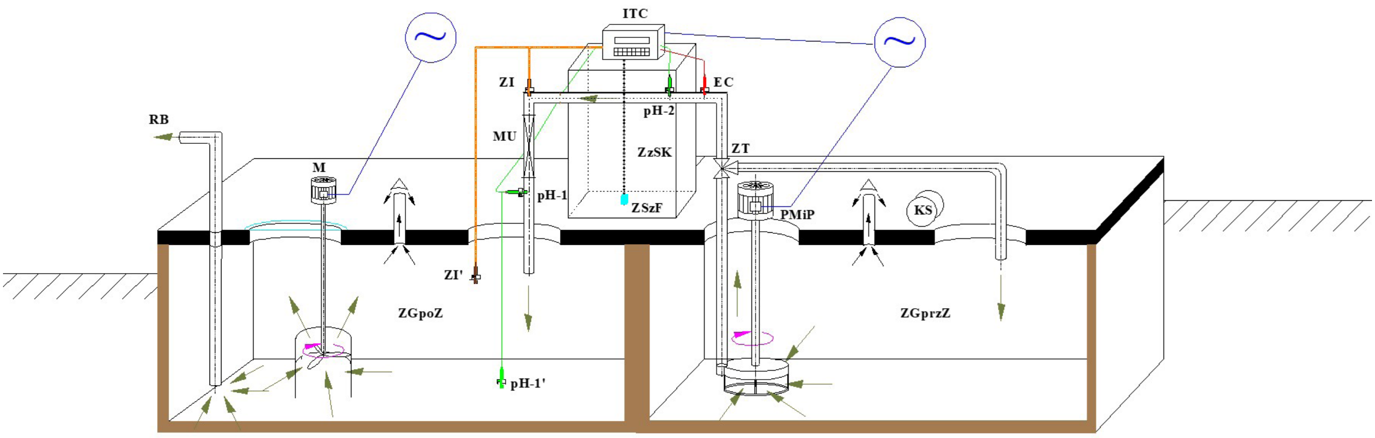

Fig. 1. Experimental pumping of fresh slurry to acidification tank
Source: Interreg 2017

ITC – dosing pump with pH meter; ZzSK – container with acid; M – mixer; PMiP – pump; ZT – three way valve; ZGprzZ – tank with fresh slurry; ZGpoZ – tank with acidified slurry; RB – discharge pipe application, as well as to increase the fertilizer value of slurry, without negative impacts on other gaseous emissions.

Figure 1 shows two concrete tanks staying side by side, one is for fresh slurry and the other for acidified slurry. These two concrete tanks are equipped in one mixer and one pump, which can be moved very easily from one tank to the other, depending on the requirements. Fresh slurry from the right tank is pumped to the left tank, where acidification occurs. Acidification process is controlled by pH meter. When process is completed, acidified slurry is taken by a tanker using discharge pipe RB.

Analysis of different storage tanks and acidification systems was provided. Also, the economic analysis concerning possible usage of acidified slurry on different crops as corn, wheat, grass etc. was carried out. Costs of energy as electricity, gas, petrol etc. were taken into consideration. Technical documentation of two concrete tanks was elaborated. To provide acidification process in the mentioned two tanks, a special automated system was elaborated. The main elements of the discussed system are: pump, mixer, pH meter, temperature meter. When slurry achieves a proper pH value then it is pumped to the tanker with trailing hoses, which will spread the acidified slurry on the field plots to provide farther experiments. After analysis of different "in storage" systems present on Danish market, there was chosen one of the systems, which can be suitable for the Polish animal herd sizes and possibility of safe acid delivery on the farm, where acidification process will be provided. This system contains the following main elements: the main frame with power transmission taken from PTO of the tractor, slurry mixer, acid pump, which delivers acid from the truck with acid to the area of slurry mixer activity, pH meter, which can check when proper PH level of slurry is achieved.

Biogas experiment concerning slurry fermentation with high dry matter content

Figure 2 shows a schematic diagram of the device, which allows to examine the individual elements of the technological process that determines the fermentation, and allows to conduct substrate fermentation studies, determine their physical and chemical characteristics, and further determine the characteristics of the fermentation process, the quality and quantity of obtained biogas and quality of digestive residues. The question of constructing a station for the production of biogas, mainly from the substrate in the form of mixture of manure, organic waste and vegetable matter was presented. The test bed according to the embodiment shown on figure 2 has a substrate fermentation vessel 1, cooperating with the pre-fermentation tank 2 and the final fermentation tank 3. The substrate fermentation tank, the pre-fermentation tank and the final fermentation tank are equipped with an insulating protective layer 5 heated by heating mantle 4. The biogas produced in these tanks is transported via lines 2 to biogas tank 24 and then to the cogeneration unit 30. During transportation to the reservoir 24, the biogas is subjected to dehydration in the trap 25 and desulphurization in the desulphurizer 26.

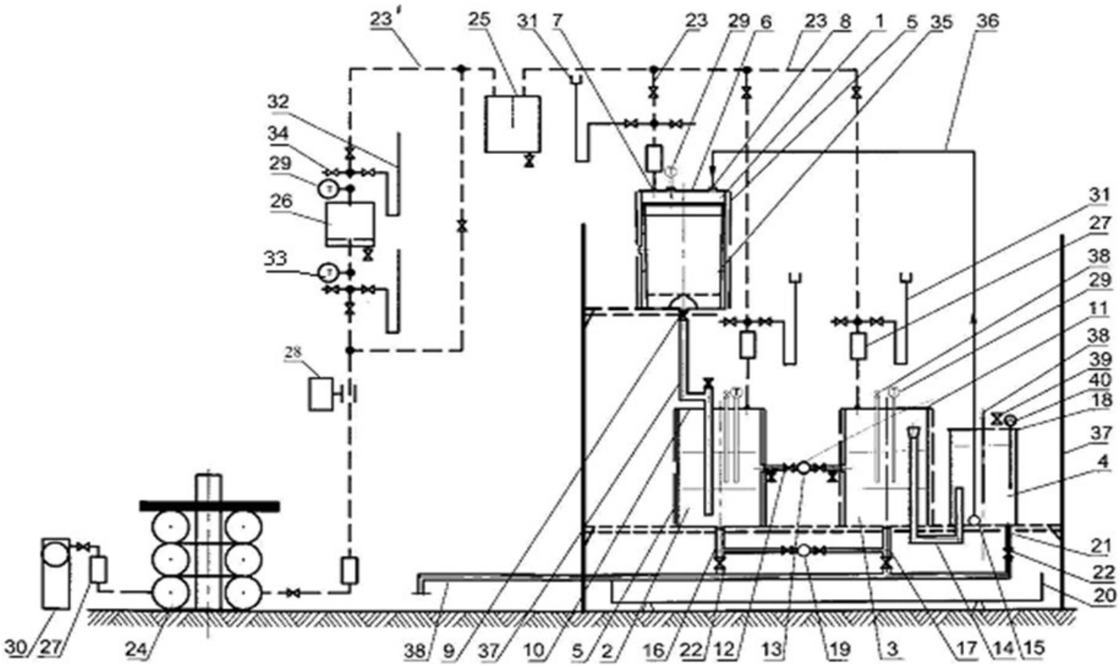

Fig. 2. Scheme of a stand for biogas recovery from substrates up to 12% of dry matter content

1 - substrate flushing tank; 2 - pre-fermented tank for rinsed organic matter; 3 - tank for final organic matter fermentation; 4 - overflow tank; 5 - external thermal insulation; 6 - tank cover; 7 - biogas feeding pipe; 8 - drain hose for rinsed organic matter; 9 - shut-off valve; 10 - tank cover; 11 - tank cover; 12 - pump; 13 - mixing pump; 14 - siphon funnel; 15 - suction-discharge pump; 16 - drain-mixing pipeline; 17 - drain-mixing pipeline; 18 – tank cover; 19 - mixing pump; 20 - bath; 21 - drain pipe; 22 - liquid organic drainage valves; 23 - biogas discharge line; 24 - biogas tank; 25 - biogas trap; 26 - biogas desulphurization; 27 - flame breaker; 28 - biogas counter; 29 - thermometer set; 30 - cogeneration unit; 31 - safety valves; 32 - biogas pressure indicators; 33 - thermometer set; 34 - biogas sampling valves; 35 - openwork basket for solid substrate; 36 - transport pipeline for rinsed organic matter; 38 - sampling slots from chambers; 39 - filler insert; 40 - liquid level indicator (Romaniuk et al., 2013)

Test results concerning fermentation process using slurry with high dry matter content

Average evaluation process parameters of fermentation mixtures tested at substrates' dry matter content equal to 10% are presented in table 1.

Table 1. Average evaluation process parameters of fermentation mixtures tested at substrates' dry matter content equal to 10% (Myczko et al., 2015)

Process parameters of fermenta-tion mixture	OS ZPE 15/15 sample 10%	PC (OS WD) ZPE 15/15 sample 10%	ST (OS WD) ZPE 15/15 sample 10%	OP ZPE 15/15 sample 10%	PC (OP WD) ZPE 15/15 sample 10%	ST (OP WD) ZPE 15/15 sample 10%	OP ZPE 15/15 sample 10%	PC (OP WD) ZPE 15/15 sample 10%	ST (OP WD) ZPE 15/15 sample 10%	K0 - inocu-lum
pH-H_2O initial TEMP. COM-PENSATION in lab. temp.: 20,5°C	**7,28** ±0,07 28,2°C	**7,32**±0,07 26,1°C	**7,31** ±0,07 26,9°C	**7,16** ±0,07 25,6°C	**7,20** ±0,07 27,8°C	**7,20** ±0,07 25,1°C	**6,94** ±0,07 24,6°C	**6,95** ±0,08 26,8°C	**6,94** ±0,07 26,1°C	**7,02** ±0,07 31,1°C
Dissolved oxygen O_2 *	0,18 [mg/l]	0,02 [mg/l]	0,06 [mg/l]	0,11 [mg/l]	0,02 [mg/l]	0,09 [mg/l]	0,13 [mg/l]	0,02 [mg/l]	0,08 [mg/l]	0,02 [mg/l]
Alkaline buf-fer potential LKT/OWN*	4,16	4,68	2,94	4,31	4,53	3,12	4,33	4,14	2,06	0,08
Loading of the fer-mentation mixture with dry organic mass	**4,54% dev** ±0,14 **68,93% dm** ±2,07	**2,60% dev** ±0,05 **69,51% dm** ±2,08	**3,57% dev** ±0,07 **67,86% dm** ±2,04	**4,51% dev** ±0,14 **68,95% dm** ±2,07	**2,53% dev** ±0,05 **69,57% dm** ±2,09	**3,47% dev** ±0,10 **68,71% dm** ±2,06	**4,20% dev** ±0,13 **69,13% dm** ±2,05	**2,49% dev** ±0,05 **67,47% dm** ±2,02	**3,34% dev** ±0,07 **69,39% dm** ±2,08	**2,68% dev** ±0,04 **67,61% dm** ±1,9
Number of fermentation days	52	4	54	52	4	56	56	4	58	14
Biogas yield SPFM**	**62,49** ±5,03 **Nl/kg dev**	**44,77** ±3,58 **Nl/kg dev**	**17,20** ±1,38 **Nl/kg dev**	**66,90** ±5,35 **Nl/kg dev**	**46,06** ±3,68 **Nl/kg dev**	**29,84** ±2,39 **Nl/kg dev**	**56,79** ±4,54 **Nl/kg dev**	**20,44** ±1,64 **Nl/kg dev**	**28,34** ±2,27 **Nl/kg dev**	**0,88** ±0,07 **Nl/kg dev**
Content CH_4 NH_3 H_2S	**53,6%** 23,6 ppm 128 ppm	**46,8%** 12,3ppm 113ppm	**51,3%** 20,2% 22ppm	**55,1%** 18,4 ppm 216 ppm	**48,8%** 18,5ppm 125 ppm	**50,5%** 12,2ppm 24 ppm	**50,7%** 8,7 ppm 34 ppm	**43,6%** 4,7 ppm 30 ppm	**50,3%** 4,0 ppm 22 ppm	**51,6%** **2,56 ppm** **9 ppm**

** Results of dissolved oxygen and alkaline buffer potential were obtained by the method beyond the scope of accreditation*

*** The result of the biogas yield is the net amount of gas from the test sample, the result of biogas yield from the inoculum is given for orientation*

Control test K0 – Inoculate methane fermentation bacteria. Lab conditions: temp. of 21.6–22.5°C, moisture. 38.9–41.6%, pressure: 1007.0–1013.0 hPa; Total drying time: 60 hours, total roasting time: 10 hours

Influence of slurry acidification on the chosen materials

To study an effect of the influence of acidic slurry on produced standard concrete samples measuring 15x15x15 cm, made from two grades of concrete C25/30 and 30/37 in an amount of 66 pieces, was carried out. As a medium, there was taken aggressive slurry acidified to a pH of 5.5. All samples after construction by the company Hydrobudowa were subjected to a process of care and maturation for a period of 28 days under the conditions specified in the standard. Then the samples were placed in an acidified slurry, normal slurry and water. Time storage of the samples in different media was set at 6 months, 12 month and 18 month. The samples will be subjected to the strength tests of concrete and, selectively, to microscopic examination of

SEM. The endurance test shall be a subject of three samples, of which the average value is calculated. The reference point is obtained compressive strength of concrete samples after 28 days of ripening and comparison with the results of the strength tests and microscopic one, conducted on the samples stored in various media for different periods of time. For laboratory tests on the effects of acidic slurry on reinforcing steel, prepared in the laboratory Hydrobudowa, the samples of concrete with embedded reinforcement were used. In the samples with dimensions 4x4x16 cm of amount 33 pieces there is placed a rod of diameter 6 mm, protected by a concrete layer with a thickness of 2 mm, 7 mm and 17 mm. The samples were placed in the media: acidified slurry, normal slurry and water. The samples will be kept for a period of 6 months, 12 months and 18 months. The measure of the impact of the corrosive action of acidic slurry will be the toughness of the samples on strength when bending. The survey will be carried out on a strength testing machine. The samples will be also a subject to macroscopic evaluation. The reference point will be the reaching of breaking strength of the concrete samples after 28 days of ripening and macroscopic evaluation of steel reinforcement. The results will be compared with the results from the research samples stored in different media for different periods of time.

Acidification of slurry is spontaneously changed, therefore, the monitoring of the level of acidity of pH and temperature was introduced.

Development of market equipment involved in slurry acidification

Mobile acidification equipment could be suitable for acidifying the slurry in storage system during mixing just before spreading. Such equipment could be invested by the farmer. Mobile equipment implies that the cost can be shared if the same equipment is used on several farms. The service could also be hired from a contractor, under the conditions that there is a contractor in the neighborhood providing this service.

Figure 3 shows the equipment, which will be delivered by ORUM Co. from Denmark.

Fig. 3. Orum Semden's "in storage" acidification system at work (farm in Denmark)
Source: ORUM Co promotion material 2017

The described professional equipment can have a big influence on farmers' interest in large size of animal herds in Poland.

Just to explain why ammonia evaporation does not exist, it can be explained by drawing the following equilibrium in slurry between ammonium salt and ammonia gas:

$$NH_{4+} + OH \leftrightarrow NH_3 + H_2O$$

At pH = 6.4 all mineralized N is found as ammonium, and no evaporation takes place.

In Denmark, the slurry should after lowering the pH <6 be spread within 24 hours according to the rules. As the spreading season lasts for longer time, this could mean a period of several weeks per year. Economical calculations are needed to compare which solution is most profitable for individual farms. When hiring the service of acidification, the technology will be available also for smaller farms. Also, if surplus storage volume is needed because of foaming when adding acid, may make the alternative non-profitable compared to the other two alternatives.

Description of processes when adding sulphuric acid to slurry is presented below:

NH_3(ammonia) + H+= NH_{4+}(ammonium)

NH_3= gas – may evaporate NH_{4+}= salt – does not evaporate)

H_2SO_4 (sulphuric acid) = Hydrogen - Sulphur-Oxygen = Sustainable

The concept of reducing slurry pH to get lower nitrogen losses to the air relies on the equilibrium between NH_4 and NH_3, what is presented in figure 4.

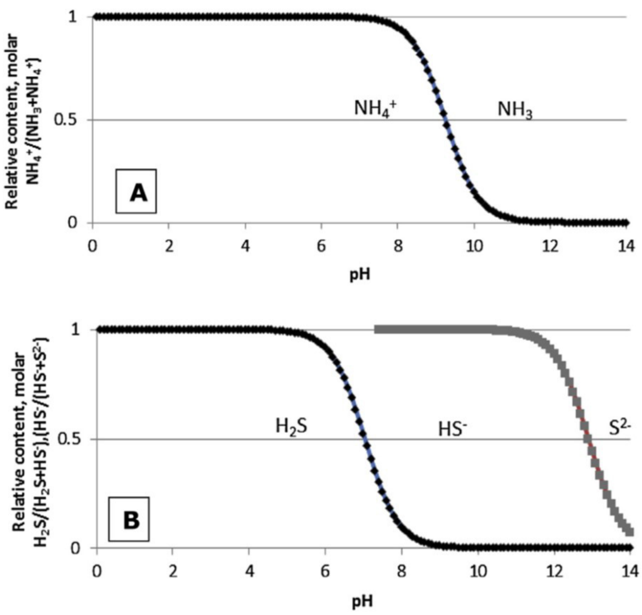

Fig. 4. Effect of slurry pH on its relative content of NH_{4+} (A) and H_2S (B)
Source: David Fangueiro 2015

Conclusions

Acidification reduces NH_3 emission from pig houses by 70% compared with the standard housing treatment. Little loss was observed from the stored slurry, and the NH_3 emission from the applied slurry was reduced by 67%. In consequence, a 43% (S.E. 27%) increase in mineral fertilizer equivalent (MFE) was measured in the field studies. The slurry acidification system is the approved Best Available Technology (BAT) in Denmark. The pH level of 5.5- 6.4 is not very acidic, and no more acidic than rain water, which has a normal pH range from 4.5 to 8.5.

Slurry acidification technology gives many advantages from the point of view of soil fertilization and also the limiting of ammonia emission. Of course it requires providing the safety procedures to avoid a direct contact of farm workers with the harmful activity of the acid. But in the case of good acidification technology, which does not allow having a direct contact either in the storage area or in the field with the acid, this job is rather safe while fulfilling the procedures.

Besides it, the discussed acidification impacts positively on other slurry treatments such as solid - liquid separation or composting; upon the use of a non-sulphur containing additive, it may also impact positively on biogas production. Nevertheless, the acidification of slurry might induce higher losses by leaching, due to solubilisation of mineral elements.

Acidification of animal slurry has proved to be an efficient solution to minimize NH_3 emissions in-house, during storage, and after soil application, as well as to increase the fertilizer value of slurry, without negative impacts on other gaseous emissions.

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