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Slurry Acidification as a Tool to Reduce Ammonia Emissions

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Abstract. Ammonia emissions are a worldwide major environmental concern. In 2017, ammonia emissions in the European part of Russia amounted to 80.9 thousand tons, of which up to 56.9 thousand tons came from agriculture. The main source of ammonia in this sector is the farm animal/poultry manure (slurry) utilisation technologies. Slurry acidification technology (SAT) is one of the methods to reduce ammonia emissions. (*Research purpose*) To assess the potential application of this technology in the Russian part of the Baltic Sea catchment area within the North-West Federal District of the Russian Federation. (*Materials and methods*) The area under study included Republic of Karelia, Kaliningrad, Leningrad, Novgorod and Pskov Regions. The authors considered the statistical data on the farm animal stock and the slurry output in the pilot area. The dynamic pattern of pig slurry pH was experimentally determined. The economic efficiency of slurry acidification technology was calculated for two functioning livestock complexes. (*Results and discussion*) According to statistical data, around 11.8 million tons of animal/poultry manure is produced in the pilot area annually, including around 7.4 million tons of slurry, which could potentially be acidified. Three SAT options – in-house, in-storage and in-field application – were considered for the Russian conditions. The main limiting factors for SAR application were identified. The SAT introduction costs and economic benefits were compared. (*Conclusions*) The prospects of SAT introduction in the pilot region were estimated. The need for the integrated research under the Russian conditions involving engineers, biologists, soil scientists, ecologists and other specialists, who could prove the feasibility and economic efficiency of the slurry acidification technology, was established.

Keywords: manure, slurry, acidification, ammonia emission, North-West Federal District of the Russian Federation.

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Подкисление жидкого навоза как один из способов снижения выбросов аммиака

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Реферат. Выбросы аммиака представляют собой серьезную проблему для окружающей среды во всем мире. В 2017 году выбросы аммиака в европейской части России составили 80,9 тысяч тонн, из которых до 56,9 тысяч тонн пришлось на сельское хозяйство. Основным источником аммиака в этом секторе являются технологии утилизации навоза животных и птичьего помета (жидкого навоза). Технология подкисления жидкого навоза стала одним из методов снижения выбросов аммиака. (*Цель исследования*) Оценить перспективы применения этой технологии в российской части водосборного бассейна Балтийского моря в пределах Северо-Западного федерального округа Российской Федерации. (*Материалы и методы*). Исследовали территорию, включающую Республику Карелия, Калининградскую, Ленинградскую, Новгородскую и Псковскую области. Авторы рассмотрели статистические данные о структуре поголовья сельскохозяйственных животных и общем количестве (выходе) жидкого навоза в пилотной зоне. Экспериментально определили динамическую картину pH навоза свиней. Рассчитали экономическую эффективность технологии подкисления жидкого навоза для двух действующих животноводческих комплексов. (*Результаты и обсуждение*) Согласно статистическим данным, в пилотной зоне ежегодно производится около 11,8 миллиона тонн навоза и птичьего помета, в том числе около 7,4 миллиона тонн жидкого навоза, который потенциально может быть подкислен. Для российских условий рассмотрели три варианта технологий подкисления жидкого навоза: в стационарных условиях, в период хранения и в полевых условиях. Определили основные ограничивающие факторы для применения технологии подкисления жидкого навоза. Сопоставили затраты на внедрение технологии подкисления жидкого навоза и рассчитали экономическая эффективность. (*Выводы*) Оценили перспективы внедрения технологии подкисления жидкого навоза в пилотном регионе. Установили необходимость проведения комплексных исследований в российских условиях с участием инженеров, биологов, почвоведов, экологов и других специалистов, которые могли бы доказать целесообразность и экономическую эффективность технологии подкисления жидкого навоза.

Ключевые слова: навоз, жидкий навоз, подкисление, выбросы аммиака, Северо-Западный федеральный округ Российской Федерации.

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In recent years, the need to improve the environmental compliance of production has become increasingly important. Owing to higher intensification, substantially more products are produced. At the same time, the increased pressure is being placed on the environment, with agriculture contributing greatly in this respect: agricultural facilities account for above 80% of ammonia emissions [1, 2]. According to the European statistics, the total ammonia emission in the EU countries steadily increased from 2012 to 2017, primarily, due to more intensive agricultural sources (*Fig. 1*).

The current Russian agriculture features the strong growth associated with the importance to ensure the food security of the country. In 2017, ammonia emissions in the European part of Russia amounted to 874.5 thousand tons against 793.7 thousand tons in 2012, of which up to 748.9 thousand tons came from agriculture against 692.0 thousand tons in 2012 (*Fig. 2*).

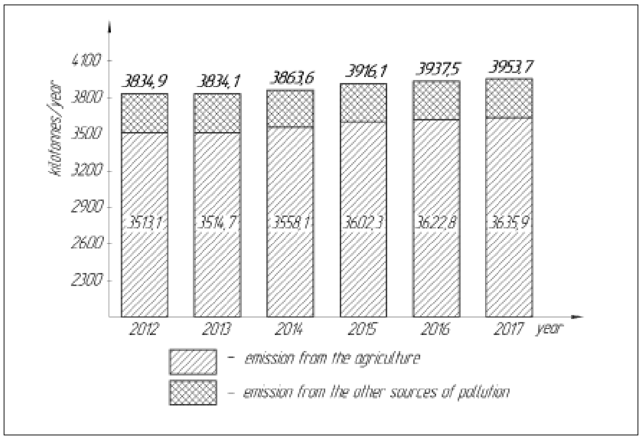

Fig. 1. Ammonia emissions in EU countries in 2012-2017 (Data from Centre on Emission Inventories and Projections – CEIP)

At the present time, the transition to the best available technologies (BAT) system as a tool to minimize the adverse environmental effect of livestock farming is underway in Russia. In farming, the animal/poultry manure utilization processes pose the main threat to the ecological balance. Available practices to reduce emissions during animal/poultry manure processing and spreading (covered storages, timely incorporation of organic fertilizers after

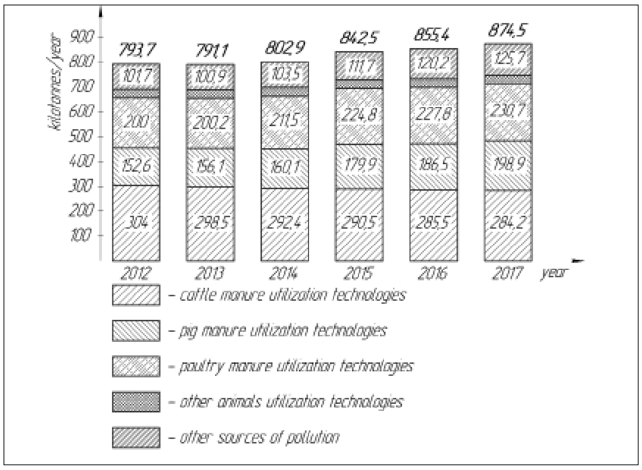

Fig. 2. Dynamic pattern of ammonia emissions from various sources in the European part of Russia in 2012-2017 (Data from CEIP)

their surface spreading, extensive use of injectors, etc.) cannot dramatically change the situation as they are not used widely enough [3, 4].

Institute for Engineering and Environmental Problems in Agricultural Production (IEEP) – branch of Federal Scientific Agroengineering Center VIM is an active participant in international projects aimed at improving the environmental compliance of agricultural production. The Institute regularly studies the foreign experience on existing and emerging practices for reducing emissions associated with agricultural organic waste processing.

Slurry acidification is one of the promising technologies for reducing ammonia emissions associated with agricultural waste processing. In recent years, this technology is becoming increasingly common in the Nordic countries. It was first proposed by S.C. Jarvis and B.F. Pain in 1990, who found that under pH values close to 5, the ammonia emission from the slurry did not exceed 1-2% [5]. The studies of various types of slurry revealed the sulfuric acid (H_2SO_4) with the concentration above 94% to be the most suitable substance for lowering slurry pH [6].

In 2016-2019 EU Interreg Baltic Sea Region project "Baltic Slurry Acidification" was implemented by 20 teams from Baltic Sea countries, with the main objective being to promote the implementation of slurry acidification techniques (SATs) throughout the Baltic Sea Region to reduce the airborne eutrophication and to create a more competitive and sustainable farming sector. Russia and Belarus were invited to participate in the project to identify the possibility of using SATs in these countries.

THE RESEARCH PURPOSE is to assess the perspectives of slurry acidification in Russia in the case study of the Russian part of the Baltic Sea catchment area within the North-West Federal District of the Russian Federation.

MATERIALS AND METHODS. The Russian part of Baltic Sea catchment area was chosen as the pilot region since the geographical and climatic conditions are much similar to other Baltic countries, which carried out a similar assessment in the framework of the Baltic Slurry Acidification project [7]. The pilot region included the Republic of Karelia, Kaliningrad, Leningrad, Novgorod, and Pskov Regions (*Fig. 3*). As of the end of 2017, the pilot region housed 2,345 thousand head of cattle, 15 thousand head of sheep and goats, over 39 million head of poultry and above 1,300 thousand head of pigs. The animal and poultry stock produced in total about 11.8 million tons of animal/poultry manure, of which 7.4 million tons (62%) were slurry and could potentially be acidified.

The economic assessment of SAT was carried out for two pig-rearing enterprises in the pilot region. The assessment results were compared with the economic effect calculated by Estonian Crop Research Institute for a pig farm in Estonia.

Experimental studies were carried out in the analytical laboratory of IEEP. The physical and chemical composition of the test samples was determined in accordance with the relevant State Standards in force in Russia. The obtained experimental data were processed by the methods of mathematical statistics.

The economic efficiency of SAT applied on a particular operating farm was calculated using a mathematical model developed by the Estonian Crop Research Institute in the framework of Baltic Slurry Acidification project [8]. The environmental impact fee was calculated following the methodology of Research Institute for Atmospheric Air Protection (Russia). The pollution fee for atmospheric ammonia emissions from manure processing facilities is calculated by the gross ammonia emission from manure during the processing and the established payment rates for ammonia emissions into the air from stationary sources by the formula [9]:

$$P_{NH_3} = G_{NH_3} \cdot S_{NH_3}, \qquad (1)$$

where G_{NH_3} – gross ammonia emission into the atmospheric air from the processing, t/year;

S_{NH_3} – payment rate for ammonia emissions into the air from stationary sources 1.95 euros/t.

The gross emission of ammonia during the processing of raw pig slurry is calculated by the formula:

$$G_{NH_3} = 31.5 \cdot 10^{-6} \cdot q_{av} \cdot y_{н} \cdot K_d, \qquad (2)$$

where G_{NH_3} – gross ammonia emission into the atmospheric air from the processing, t/year;

q_{av} – average filling of manure storage facilities per year, t;

$y_{н}$ – specific ammonia emissions from pig manure into the air, microgram/t dry matter;

K_d – wet to dry matter conversion factor;

$31.5 \cdot 10^{-6}$ – conversion factor of microgram/s to t/year.

The gross emission of ammonia during the processing of the liquid fraction of pig slurry is calculated by the formula (3):

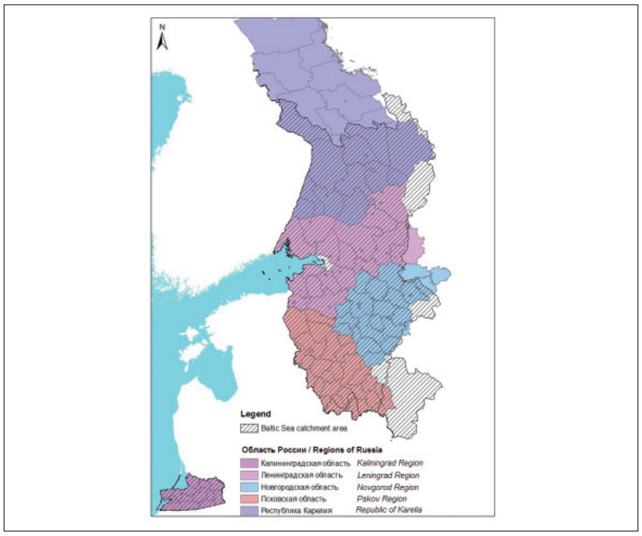

Fig. 3. The pilot region for assessing the potential application of SATs in Russia – the Russian part of the Baltic Sea catchment area

$$G_{NH_3} = 31.5 \cdot \sum_{n=1}^{N_u} P_n M_{n,i,j}, \qquad (3)$$

where N_u – the number of selected gradations of the average wind speed u related to the standard height of the weather vane $z_ф = 10$ m;

P_n – dimensionless (in fractions from 0 to 1), repeatability of *n*-th gradation of wind speed;

$M_{n,i,j}$ – emission rate of the substance in question from the *j*-th source for the concentration and the average wind speed u, assumed to be equal to the mid-point of the *n*-th gradation, g/s;

31.5 – conversion factor of g/s to t/year.

RESULTS AND DISCUSSION. The main slurry processing technique in the region under consideration is the long-term storing (maturing) – above 90% of agricultural enterprises consider it as a basic slurry utilisation technology. The widespread use of this technique would make it possible to introduce SAT in the storage facilities with their minor reconstruction. However, the specific national feature is that manure storages are much larger than those used in the Baltic Sea countries; therefore, the homogenization of acidified slurry would be challenging.

About 90% of the liquid organic fertiliser produced from slurry are applied by spraying. In 2012-2017, the share of band spreading increased significantly from 2% to 9% of the total liquid fertilisers applied. The remaining application techniques account for 3-4% (*Fig. 4*). Above 60% of the liquid fertilizers are applied for supplementary fertilization of perennial grasses; 40% of the liquid fertilisers are applied during the ploughing before the perennial and arable crops seeding and incorporated within 1-2 hours after application.

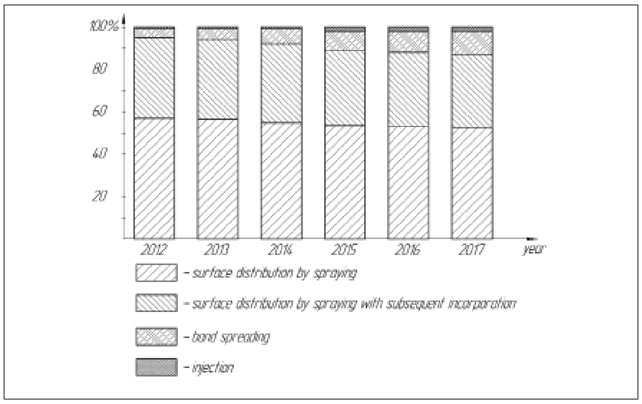

Fig. 4. Share of different application techniques of the liquid organic fertilizers produced from slurry in the pilot region (Data from CEIP)

Three options of SAT are distinguished [6, 10]:

- In-house acidification: the sulfuric acid is added to slurry in a covered treatment tank outside the livestock house under stirring to reach a fixed *pH* level of 5.5. Part of acidified slurry is returned to slurry channels, where it mixes with the new slurry, and part is discharged to the storage. The average application rate of the acid is 3-4 litres per one ton of slurry.
- In-storage acidification: the acid is added to the storage tank or lagoon under heavy mixing to reach a pH level of 6. Much foam is produced upon the addition, and its removal is the main constraint of this acidification option. The entire amount of slurry may be acidified in the main storage or a part of it is intensively acidified in the buffer tank and mixed with the slurry in the main storage. The acid consumption is 2-3 litres per one ton of slurry.
- In-field acidification of the slurry: the acid is added to the slurry immediately before the soil application, in a static mixer installed in the output of the slurry tanker. The acid consumption is 1.5-2.5 litres per one ton of slurry to reach the pH of 6.4.

SAT is widely used in Denmark. Today, about 16% of all slurry produced in Denmark is SAT-processed [11]. During the field trials in Sweden in 2016-2017, the acidified slurry application contributed to 22.2% higher green mass yields compared to reference and 8.6% higher green mass yields compared to the non-acidified slurry application [12, 13]. This increase is owing to better nitrogen saving in the acidified slurry, and, accordingly, its greater nutritional value.

Our studies showed that under conditions of the North-West Federal District of the Russian Federation the in-field acidification was the most technically feasible technique, however it required the substantial upgrading of the available machine and tractor fleet [14]. The increased wear of equipment, associated with the high acidity of applied slurry, and higher qualification requirements for the personnel involved should be taken into account as well. The main challenge in introducing this slurry acidification technique may be the serious safety requirements for transportation and use of aggressive acids, sulfuric acid included.

The in-house acidification is also challenging, as on the operating livestock farms the pumping of slurry back to the livestock house is not technically feasible. Moreover, there are several regulatory restrictions to this process. However, in some special cases, for example, when a flash-flume system is used, this technique can be successfully implemented.

The next stage of the work was the laboratory analysis of pig slurry samples, their physical and chemical composition (*Tab. 1*). Sample 1 was non-separated pig slurry taken at the exit from the pig house; Sample 2 was the liquid fraction

Table 1

PHYSICAL AND CHEMICAL COMPOSITION OF THE SLURRY SAMPLES UNDER STUDY

Indicators	Sample 1	Sample 1
Dry matter/, %	13.0	3.5
pH	8.1	6.4
N_{total} content, % Including ammonium nitrogen	0.840 0.495	1.540 0.477

of the pig slurry taken at the outlet of the separator. The samples were taken within 48 hours prior to the study.

The dry matter content in the test samples was determined by drying in accordance with the State Standard GOST 26713-85 “Organic fertilizers. Method for determination of moisture and dry residue”; the acidity (*pH*) was determined using Expert-001 3 (01) fluid analyzer in accordance with the State Standard GOST 27979-88 “Organic fertilizers. *pH* determination method”; Ntotal content was determined by the photometric method in accordance with the State Standard GOST 26715-85 “Organic fertilizers. Methods for determination of total nitrogen”; the ammonium nitrogen content was determined using an Expert-001 3 (01) fluid analyzer in accordance with the State Standard GOST 26716-85 “Organic fertilizers. Methods for determination of ammonium nitrogen”.

To reduce slurry *pH* to 5.5, the sulphuric acid with 96% concentration was added to Sample 1 at the rate of 3.7 l/m^3, and to Sample 2 at the rate of 1.2 l/m^3. (*Fig. 5*).

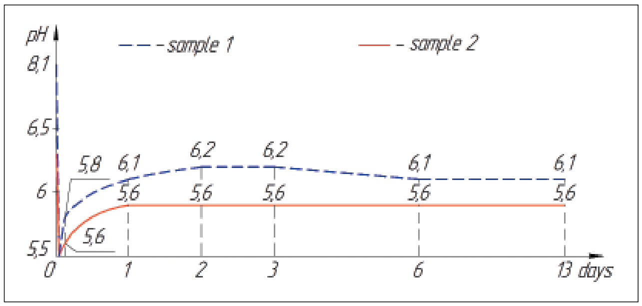

Fig. 5. Pattern of pig slurry pH change during the experimental study

A gradual *pH* increase was observed during the first day up to 6.1 (Sample 1) and 5.9 (Sample 2). No significant fluctuations were observed during the rest 12 days. This may support the assumption about the key role of the uniform acid distribution over the entire volume of the treated slurry in order to eliminate or minimize the re-acidification. The higher *pH* of Sample 1 after acidification was caused by the higher dry matter content of slurry compared to Sample 2 (*Tab. 1*). The dry matter has *pH* buffering effect after the slurry acidification.

A decrease in the ammonia emission was also established. However, additional research is required over a longer time-period to obtain the reliable data. At the same time, significant foaming when adding the acid to the slurry should be considered. This occurs, presumably, as a result of gas emission during the decomposition of carbonates. This issue also requires additional investigations.

To estimate the annual economic effect of the in-storage SAT application, the ECRI mathematical model was used. This effect is based on the condition that SAT application will save more nitrogen in the organic fertilizer and increase the sulfur content, thereby reducing the purchasing costs of relevant mineral fertilisers. The annual economic effect was calculated for the entire technological chain: animal housing system, slurry storage and processing systems, and slurry application technique (*Tab. 2*).

The estimated economic effect of SAT introduction is defined as the difference between the costs related to preparation and application of organic and mineral fertilizers in order to obtain the target yields by the traditional technology and using an additional slurry acidification unit. At the same time, the SAT introduction costs are offset by the reduced requirement for nitrogen and sulfur application with the mineral fertilizers through the lower loss of ammonium nitrogen and higher sulfur content in the slurry. Nitrogen loss reduction and corresponding slurry nitrogen content increase is calculated for the entire production cycle with due account for the applied environmental measures, for example, covered storages, slurry injection, etc.

The economic effect of the in-storage SAT introduction was calculated for two Russian pig-rearing complexes.

The first pig complex had the animal stock of 105,000 head and the complete production cycle including the long-term slurry storing (maturing) in film lagoons. The complex applies the technology of non-separated (raw) pig slurry processing. The estimated SAT introduction costs would be 122,375 euros per year. According to formulas (1) and (2), the pollution fee is 164 euros per year that is 747 times lower than the SAT introduction costs.

The second pig complex had the animal stock of 108,000 head and the complete production cycle, with the slurry being separated into fractions and the long-term storing (maturing) of the liquid fraction in concrete lagoons and the passive composting of the solid fraction in piles. The estimated SAT costs of the liquid fraction would be 42,689 euros per year. According to formulas (1) and (3), the pollution fee is 8.88 euros per year, i.e. 4,800 times lower than the SAT introduction costs [15].

The results obtained were compared with the similar calculation for a pig farm in Estonia made by Estonian Crop Research Institute. The cost-effectiveness of SAT calculated for a fattening pig farm with the animal stock of 40,000 head located in Estonia and governed by EU Directives amounted to 44,000 euros per year achieved, primarily, by reducing the cost of mineral fertilizers purchased.

CONCLUSIONS

The study performed in IEEP – FSAC VIM demonstrated the certain promise of the slurry acidification technology application under conditions of the pilot region, where 7.4 million tons of slurry are produced annually. The available material and technical facilities allow for SAT introduction if they are upgraded.

According to the preliminary analysis of the situation in the agricultural sector and current relevant legislation, the in-storage and in-field slurry acidification options had more prospects for the introduction. The economic efficiency estimation, however, revealed the lower cost of mineral fertilizers purchased for crop and fodder production to be the key factor affecting the SAT attractiveness. When the

Table 2

Estimation the economic effect of SAT introduction

Indicators	**Values**	
	Russian Federation	**Estonia**
Capital costs of SAT introduction	ØrumSmeden equipment set, which is a system for the acid supply from the tank to the storage; mounted on a mixer.The cost is 14,000 euros per set	
Operating costs:		
maintenance costs	60 euros per year	60 euros per year
labour costs of service personnel	at a wage rate of 3.6 euro per hour, the labour costs to process 1 m^3 of slurry are 0.002 euros	at a wage rate of 7.39 euro per hour, the labour costs to process 1 m^3 of slurry are 0.005 euros
fuels, lubricants and electricity costs associated with slurry acidification	0.36 euros per 1 m^3 of slurry	0.59 euros per 1 m^3 of slurry
Other costs:		
purchase costs of work clothes, protective devices	160.55 euros per year	160.55 euros per year
additional costs associated with slurry storage*	0.01 euros per 1 m^3 of slurry	0.01 euros per 1 m^3 of slurry
purchase and transportation costs of nitrogen-containing mineral fertilisers	523 euros per ton of mineral fertiliser nitrogen	720 euros per ton of nitrogen within mineral fertilisers
purchase and transportation costs of sulfur-containing mineral fertilisers	150 euros per ton of mineral fertiliser sulphur	148 euros per ton of mineral fertiliser sulphur
additional soil liming costs**	20 euros per ton of dolomitic meal	16.7 euros per ton of lime
sulfur acid purchase costs associated with slurry acidification	0.155 euros per litre of acid	0.216 euros per litre of acid

* Due to intensive foaming, the additional storage volume is to be provided for when constructing the storage facilities that increases the maintenance costs of the operating storage;

** Theoretically, 1 to 1.8 kg of lime per liter of acid consumed is required depending on the soil type. The actual need for liming also depends on the soil properties. The project field experiment results did not show the significant soil acidification due to the use of acidified slurry

primary objective of the farm is to utilize the manure produced without the possibility of growing a part of the fodder on its own fields, the SAT costs are many times higher than the economic effect of lower pollution fees.

Along with the advantages of SAT introduction, several limiting factors should be noted:

- stricter requirements for working with especially hazardous substances and precursors, namely sulfuric acid;
- the need for additional liming of soils at the estimated rate of 1.0-1.8 kg of lime per 1 liter of acid.

Taking into account the current environmental legislation and the low interest of livestock enterprises in the more efficient use of organic fertilizer nitrogen produced, SAT introduction seems somewhat premature in Russia. The positive experience of using this technology in the EU countries, however, allows attributing SATs to the realizable technologies. The transition to BAT system, which would govern the activities of large-scale pig and cattle complexes in Russia, suggests that in the near future, the interest in such technologies should increase. At the moment, the livestock complexes are more concerned about the reduction of odorous emissions than in lower nitrogen loss.

As Russia does not have the experience in SAT application so far, the integrated research is required under the Russian conditions involving engineers, biologists, soil scientists, ecologists and other specialists who could prove the feasibility and economic efficiency of this slurry treatment technique.

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