Integration of Technologies: Biogas Production, Fertilizer Production and Biogas Upgrading

O. Sokk*, E. Loigu*, R. Kuusik, A. Menert*****

*Institute of Environmental Engineering, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia (E-mail: *olevsokk@hotmail.com and enn.loigu@ttu.ee*)
**Laboratory of Inorganic Materials, Tallinn University of Technology (E-mail: *rein.kuusik@ttu.ee*)
***Department of Chemistry, Tallinn University of Technology (E-mail: amenert@cc.ttu.ee)

Abstract
This paper presents principle technology to produce suspension fertilizer based on wastewater treatment plant excess sludge and alkaline oil shale ash from a thermal power station. For that the treatment in a mechanical disintegrator and contact with biogas from the anaerobic process of wastewater excess sludge is used. The ash is responsible for *hygienisation* or diminishing of intestine micro-flora in mixture. To get a suspension fertilizer and ensure total *dehelminting* sludge-ash mixture held together in a time and after that must be mechanically co disintegrated with mineral fertilizers. The latter is responsible for increasing nutritional value of the suspension. Dehelminting is achieved via the mechanical friction of helminthes eggs and damaging these by collisions with high velocity broken pieces of non-soluted mineral solids. Contact with biogas reduces high pH level of suspensions. At the same time it is a reasonable method for the upgrading of biogas.

Keywords
Excess sludge; ash; disintegration; suspension fertilizer; biogas upgrading

INTRODUCTION

The objective of the article is to give an overview of how to prepare suspension fertilizers from wastewater treatment plant excess sludge and shale ash by mean of integration different technologies. Suspension fertilizers are mixtures of liquid, stabilisation matter, dissolved and non-dissolved mineral nutrients. Stabilisation material commonly has a clayish nature and it assures holding the non-solute fertilizer particles homogeneously in suspension. Clay or similar matter is generally substitutable by non-settle able excess sludge that originates from activated sludge treatment plants. Applicable sludge content of dry solids has to be around 4% (≥40g L^{-1}) and may reach to higher values (6-8%). When excess sludge and shale ash are used together in the mass, the concentration of sludge may be less. Even 20 g L^{-1} may be sufficient. The sludge must not contain viable helminth eggs. If needed the dehelminting process can be carried through by mechanical disintegration.

Disintegrator (Hint, 1981) is a mill where oppositely placed discs are equipped with milling elements (Figure 1). These are positioned in intermeshing circles. The material to be ground is directed to the centre. By the centrifugal force the material is forced outwards through the counter-rotating milling elements. Collision velocity between material particles and milling elements depends on the rotating speed and element placement radius and may reach 300 m s^{-1}. It was assumed that in such highly energetic mechanically agitating environment helminth eggs would be damaged and loses germinating ability. Such treatment is not sufficient to decrease the viability of infectious bacteria and therefore separate treatment to degrade bacterial germinating is needed. Utilization of shale ash in the mixture of suspension fertilizers raises the level pH and that suppresses the viability of the micro flora.

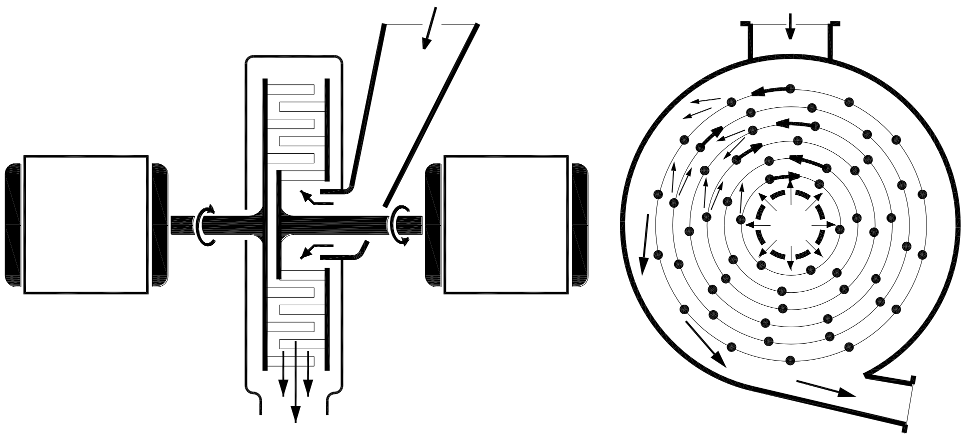

Figure 1. Principles construction of disintegrator with motors on the left and treatment process is featured on the right (according to Hint, 1981).

METHODS and MATERIALS

Pilot plant dehelminting experiments were carried out in Uzbekistan on a disintegrator of 1,2 m rotor diameter and a rotation speed 1500/1500 min^{-1} (impact velocities ≤ 185 m s^{-1}). Local specialists in the laboratory of the Tchirchik wastewater treatment plant have counted of helminth eggs in samples, which had a volume one litre. The method was known and accepted at that time in the former USSR. In high concentrated salt solution the eggs float to the liquid surface from where they are gathered and countered under a microscope. Infection tests on guinea pigs were accomplished in the Hygienic Institute in Samarkand.

Experiments to reduce the concentration of viable intestine micro-flora was carried out in Tallinn University of Technology on a 35 cm rotor diameter disintegrator at a rotation speed 3000/3000 min^{-1}, which gave an impact velocity 110 m s^{-1}.). The concentration of viable intestine micro flora was determined as the number of CFU (colony formed units) per one gram of suspension. This number was determined for *Escherichia coli* as the representative of intestine micro flora and indicator of contagiousness. CFU was measured by the method of most probable number in the microbiology laboratory of Estonian Environmental Research Centre. The value of the pH was received by measuring the sludge water solutions (1:5). Contacting**.** Certain quantities of tests between suspension fertilizers and biogas were carried through in a hermetically closed plastic bottle biogas and suspension fertilizers were introduced into the bottle. These components were shacked 3-5 minutes. The bottle had a hose connection with a vessel containing liquid or suspension. It was necessary for the elimination of the vacuum created by absorbed CO_2 in the bottle. Biogas was obtained from an anaerobic reactor treating the liquid wastes of a yeast factory.

Anaerobic testing of different liquid wastes originated from food industries were carried through at a laboratory anaerobic digester (Armfield, 1995), which had controllable input and temperature regulation. According substrates for testing were obtained: cheese whey from Võru dairy industry in the south of Estonia, distillery waste from Rakvere alcohol distillery factory (location in the north-east of Estonia), vegetable oil production wastes were created in the case of elaboration of the technology for getting oil from rape seed. With elaboration the technology was engaged Institute of Chemistry of Tallinn University of Technology.

EXPERIMENTS and DISCUSSION

For producing suspension fertilizers with excess sludge as the stabilizing matter the technology was developed in years 1986-1990 and put into pilot scale use in Central–Asia. There the use of aerobically stabilized excess sludge as organic fertilizer was relatively popular with the local population. However the sludge has a very high concentration of helminth eggs (hundreds per litre). For the dehelminting of sludge mechanical disintegration was investigated.

Experiments without mineral nutrients were carried out in excess sludge solid concentrations of 2-4% and with minerals in concentrations 6-10%.

Between rotors material is subjected to collisions and shear forces. The relations between shear- and impact forces depend on the construction of the rotors. Different rotors were tested. A detailed description of their technical peculiarities is not the goal of this article and naming of rotor types has formal importance. The results of sludge dehelminting experiments for a throughput of 5 m^3 h^{-1} are summarised in Table 1 (Loopere *et al.*, 1987).

Table 1. Characteristics of experiments.

Variant	Type of rotor	Material treated and dry solid content in sludge	Efficiency of dehelminting, %	Specific energy consumption, kJ kg^{-1}
1	Finger shaped	Sludge 2-4%	85	140
2	Ribbon	Sludge 2-4%	50	75
3	Radial mono	Sludge 2-4%	70	22
4	Finger shaped mono	Sludge 2-4%	65	25
5	Blade	Sludge 2-4%	88	72
6	Blade	Sludge 6-8% and minerals	100	72
7	Blade densified	Sludge 2-4%	96	60
8	Blade densified	Sludge 6-8% and minerals	100	60

Variants 1, 2, 3, 4, 5 and 7 represent experiments where excess sludge dry solid content was 2-4%. A difference in energy consumption and dehelminting efficiency was observed, but entire dehelminting was not achieved. Variants 6 and 8 represent the making suspension fertilizers. Higher sludge solid concentration held non-solute mineral particles in suspension. Entire dehelminting was achieved. Parallel fertilizing trials with the same quantity of mineral nutrients, in one case as dry solid and in the other case in suspension were accomplished. In Uzbekistan on-field productivity increase lied in the range of 3-9% in the case of onion, tomato and maize cultivation. A few samples from sludge containing 15-25 % helminth eggs after treatment, were sent to laboratory to investigate the viability of the remained eggs. Infection tests on guinea pigs showed that if the eggs of untreated sludge had infectiousness over 90% then the eggs from treated sludge had lost this capability.

As the experiments were carried through in Uzbekistan in the year's 1986- 1987, other characteristics the concentration of heavy metals and of intestine microbes was not considered. New experiments to create suspension fertilizers, on basis of no stabilized wastewater treatment sludge, were launched in the autumn of 2006 (Sokk *et al.*2007). For the stabilisation of the waste sludge and the reduction of intestine micro flora oil shale ash, obtained from thermal power station, was used. At the present time there are no problems with helminth eggs in Estonia. In Tallinn wastewater sludge only single eggs in few sludge samples have been discovered and average permissible number of helminth eggs number of one per litre is all the time fulfilled. Concentrations of heavy metals in sludge and ash were considered. In principle it was revealed that their mixture could be used as fertilizer if the concentration of heavy metals is not significant. (Table 2). Therefore the objective of the experiments was how to reduce the number of *Escherichia coli* (Table 3). Permissible number of CFU for *Escherichia coli* has to be no more than 1000 per 100 ml sludge suspension.

Table 2. Concentrations of heavy metals in dry solids, mg /kg.

Metal	In sludge	In ash	In mixture*	Permissible in sludge
Cd	0.73–6.0	0.19–3.5	≤ 4	20
Cu	77.3–700	5.6–17.9	≤ 132	1000
Ni	10.2–200	19	≤ 50	300
Pb	21.7–98	13.4–383	≤ 340	750
Zn	519–1120	284	≤ 425	2500
Hg	0.87–1.7	1	≤ 1.2	16
Cr	11.4-180	15.5–58.6	≤ 80	1000

*Calculated as maximum for dry mixture that is derived from raw mixture with 40% dry ash and 60% raw sludge containing 8% dry solids.

Table 3. CFU g^{-1} of *Esherichia coli* in suspensions.

	CFU measured		pH	Dry solids %	Experiment
	Day of disintegration	After 3 days			
Natural sludge	3 155 354		7.11	6.63	First
Natural sludge disintegrated	13 220 556		7.25	4.67	
Mixture (sludge 60%, mineral fertilizer 40%) disintegrated	18 071	11 556	5.65	41.5	
Mixture (sludge 60%, fertilizer 32%, ash 8%) disintegrated	54 361	11 556	6.86	41.5	
Natural sludge disintegrated	19 259 046		6.91	6.5	Second
Mixture (sludge 60%, fertilizer 20%, ash 20%) disintegrated	15 196		8.36	37.7	
Mixture (sludge 60%, fertilizer 10%, ash 30%) disintegrated	198		9.19	41.9	
Mixture (sludge 60%, ash 40%) disintegrated	<12.3		12.26	45.5	

Calculated CFU in raw sludge on the two last variants in the table 3 gives 8300 and <560 per 100 ml respectively.

On the basis of table 3 the following conclusions can be drawn:

1. Disintegration is not a diminishing factor for CFU in waste sludge
2. Prolonging the contact time between the components of sludge mixture diminishes CFU.
3. The main-diminishing factor of the CFU in sludge mixture is a pH of over 12. Then the required number of CFU is achieved.

It was concluded that disintegration of the sludge with mineral fertilizers has a great significance for the dehelmintisation but not for the hygienisation in regard to intestine bacteria. The hygienisation is available to achieve via the increasing of the sludge mixture pH. So far the preparing of the fertilizer mixture and its disintegration was accomplished simultaneously. The process was completed in about half an hour. Table 3 indicates both that the presence of mineral fertilizers decreases the mixture pH and only comparatively high ash concentrations can increase this value. Tests to reveal the influence of the ash concentration and its contact time to pH value without fertilizers are presented in table 4.

Table 4. CFU g^{-1} of *Esherichia coli* in the mixture of waste sludge and shale ash.

Ash %	CFU measured		pH	Dry solids %
	After 1 day contact time	After 4 days contact time		
Natural sludge	214 720	50 384	6.81	2.17
2.5	240 800	4582	8.99	5.29
5	621	925	10.58	6.72
10	23	<5.6	11.58	12.4

To sludge, that contained 10% ash had a contact time of 4 days with it, were added different mineral fertilizers. The fertilizers concentration were maintained 20% in the suspensions. From these mixtures the CFU of *Esherichia coli* was determined. The results are presented in table 5.

Table 5. CFU by different fertilizer suspensions.

Fertilizer	Dry solids %	pH	CFU g^{-1}
Ammonium nitrate	29.8	7.43	<5.6
Sodium nitrate	30.8	10.59	<5.6
Superphosphate	28.5	6.63	<5.6

Table 5 indicates that in the mixture of sludge, ash and mineral fertilizer chemical processes took place, as with every different fertilizer resulted a different pH. This phenomenon would have no influence to CFU if the contact time between ash and sludge had been sufficient before fertilizers were added. Hereby all CFU stayed under the determination threshold.
The decreasing of the pH takes place first of all in the case if mixture contains NH_4^+ ions, but in the case when it is absent (for instance sodium nitrate in our case) the falling of pH is insignificant and therefore the neutralization of the fertilizer suspension is recommended.

In Estonia the electric power production is based on the combustion of local low-grade carbonaceous fossil fuel – oil shale, results in large-scale formation of lime-containing ash and high CO_2 emissions by flue gases (specific carbon emission factor is as high as 29 tons of carbon per TJ of produced energy) (Kuusik *et al*. 2005; Kuusik *et al*. 2005). The possibilities of the ash forming in the process of oil shale combustion to capture the carbon containing in the flue cases were investigated (Uibu *et al*. 2007). Waste ash suspension in water was prepared and flue gases were barbotaged throw it. Satisfied results for absorption of CO_2 in ash suspension were gained (Uibu *et al*. 2009). This phenomenon is in tight connection with the suspension pH and in the process of CO_2 absorption the pH is dropping down (Uibu *et al*. 2010). This knowledge encouraged to examin this principle in case of suspension fertilizers where the source of CO_2 is biogas (Sokk *et al*. 2008).

In the contacting tests the initial volume ratio of the biogas and suspension fertilizer was 4 : 1. The nutrition component in the suspension was sodium nitrate ($NaNO_3$) in a mass concentration of 20% and ash concentration of 10%. The average values of three repeated tests were:
1. The concentration of CH_4 increased from 57% to 93.5% with a variation of <3%.
2. The pH of suspension fertilizer dropped from 12.23 to 10.05.
3. By smelling the concentration of hydrogen sulphite (H_2S) and other malodorous components was obviously decreased. Instrumental analysis didn't show the presence of H_2S.
4. When treated suspension fertilizers with pH 10 - 11 were barbotaged again in previous conditions the pH continued the dropping and got new values 7.2 – 7.5.

Considering above presented, it is clear that lowering the pH by means of biogas will cause its purification and increase in its calorific value. This linked together with suspended fertilizers production can be regarded as a method for biogas upgrading for use as a consumable energy carrier. In this case the biogas productivity become important and it is reasonable to treat liquid wastes of high organic concentrations anaerobically. Wastewaters from different food production industries have high BOD and COD concentrations. In our institute anaerobically tested wastewaters originated from cheese and vegetable oil production and alcohol distilleries (Blonskaja *et al.* 1999; Blonskaja *et al*. 2006).

The short review of these experiments is presented in the table 6.

Table 6. The main investigated parameters of the anaerobic treatment processes.

Reactor type	Origin of wastewater	HRT days	Load, kg COD $m^{-3}d^{-1}$	COD input	COD removal %	Energy produced $kJ/m^{-3}d^{-1}$
Contact process[0]	Cheese whey	5-10	4.32-18.28	60 300 - 66 700	40-83	78.2
UASB[0]	Cheese whey	2.5-12	0.5-16		58-98	72.4
Fixed bed[0]	Distillery	10-19	2.5-5.1	49 000 - 53 000	≤54	≤23.1
UASB[0]	Distillery	20-39	0.6-2.5		≤93	≤16.2
Fixed bed[0]	Vegetable oil	7-90	0.1-2.2	6 700 – 11 000	≤85	≤11
Fixed bed[1]	Vegetable oil	1-1.5	6-9		≤85	≤71.7
Fixed bed[2]	Vegetable oil	3-4	1.6-2		≤85	≤17.2

[0]Single stage reactor

[1]First stage anaerobic reactor

[2]Second stage anaerobic reactor

Considering the average values of 4th and 6th columns in the table 6, the 7th column for potential energy production is created. Hereby the facts that one kg CH_4 corresponds to four kg COD and combustion (oxidizing) of one kg CH_4 produces 50 kJ energy was taken into account. In the calculations it was assumed that 10% of COD removal was caused by anaerobic biomass synthesis. The COD removal in case of cheese whey was calculated on the basis of median values of COD.

The stored potential energy per unit mass (kJ kg^{-1}) for petrol and methane are accordingly 4.4×10^4 and 5.0×10^4 and specific gravity of petrol is 0.73 – 0.78 kg L^{-1}. This means that in terms of contained potential energy, one kg methane corresponds to 1.5 litres of petrol or that the energy contained in one litre of petrol can be obtained by removal of three kg of COD in anaerobic process.

In principle, it is possible to reduce significantly waste sludge, ash and high-concentration wastewater pollution. At the same time, mineral organic suspension fertilizer is obtained and biogas as an alternative energy carrier is upgraded. An advantage of this is also that by barbotageing with biogas a part of the CO_2 that is released early is captured, as carbonates and the "greenhouse effect" is retarded. In the above-mentioned waste treatment technologies only one marketable material is used that is real mineral fertilizer.

The presented tests do not resolve the problem entirely they demonstrate the possibilities and ways for the resolving problems related to the reduction of environmental pollution.

CONCLUSIONS

The possibility of getting a new valuable product from different waste materials by combining treatment technologies including disintegration has been shown.

A special rotor construction is required and a simultaneous disintegration of the sludge and mineral nutrients is needed for complete dehelminthing of excess sludge. Specific energy consumption to achieve complete dehelminting is around 70 kJ kg^{-1}. For hygienisation (decreasing CFU intestine micro-flora to required level) an increase of suspension pH to >11-12 is necessary. These levels of suspension pH are attainable by adding oil shale ash (obviously other kinds of ash are applicable). The difference of acceptable ash concentrations must be emphasized. When ash is added before the fertilizer and its contact time 4 days is provided, and then a 10% ash concentration suffices. However, when ash and the mineral fertilizer is added to the sludge practically simultaneously, then an adequate ash concentration may have to be several times higher. Combining waste sludge, ash, mineral nutrients, contact time and mechanical disintegration in different proportions nutritionally valuable and environmentally hygienic safety suspension is attainable. By means of disintegration extremely homogeneous, fine and entirely dehelminthed suspension is received. This suspension containing waste sludge and ash is considered a bio solid, but containment of mineral nutrients makes it more valuable and it is regarded as suspension fertilizer**.** In the case when after disintegration the pH of fertilizer suspension is too high the treatment of suspension with biogas drops it and the quality of the biogas as energy source improves. Especially valuable would be to integrate suspension fertilizer production with simultaneous anaerobic treatment of high concentration waste liquids from foodstuff production. Using the suspension in land cultivation requires following the legislation concerning heavy metals.

REFERENCES

Blonskaja, V., Mölder, H., Sokk, O., and Vaalu, T. Investigation of anaerobic treatment of extremely high concentrated waste in the cheese industry. HELECO ´99, Environmental Technology for the 21st Century, 3rd International Exhibition & Conference, 3-6 June 1999, Thessaloniki, Greece, 57-62

Blonskaja, V., and Vaalu, T. (2006). Investigation of different schemes for anaerobic treatment of food industry wastes in Estonia. Proc. Estonian Acad. Sci. Chem., 2006, **55,** 1, 14-28

Hint J. (1981). UDA- technology: problems and perspectives. Special Construction-Technological Bureau "Desintegrator". Tallinn "Valgus" 1981, pp.35. (in Russian)

R. Kuusik, M. Uibu, K. Kirsimäe. Characterization of oil shale ashes formed at industrial-scale CFBC boilers. *Oil Shale,* 2005. Vol. 22, No. 4 Special. P. 407-419.

Kuusik R., Uibu M., Toom M., Muulman M.-L., Kaljuvee T., Trikkel A. (2005) Sulphation and carbonization of oil shale CFBC ashes in heterogeneous systems. *Oil Shale*, Vol. 22 No 4 Special pp.421-434

Loit H., Loopere V., Solovjov P. V., Tümanok A. and Birgelis A. (1989) Disintegrator method of preparing complex suspension fertilizers. Scientific-Industrial Concern "Desintegrator". Disintegrator Technology: Thesisies of presentations on 6. All-Union workshop 5-7 Sept, Tallinn, pp.117-119. (in Russian)

Loopere V., Loit H., Tümanok A., Solovjov P. V., Karmazin V. M. and Babajeva R. I. (1987) Dehelminting of wastewater sediments. Scientific-Industrial Concern "Desintegrator". Disintegrator Technology: Thesisies of presentations on 5. All-Union workshop 8-10 Sept, Tallinn, pp.165-167. (in Russian)

Sokk, O. and Goljandin, D. (2007) Suspension Fertilizer from Excess Sludge. Conference proceedings: Facing Sludge Diversities: Challenges, Risks, and Opportunities; 28-30 March, 2007 Antalya, Turkey, 971-974

Sokk, O., Kuusik, R. Loigu, E. (2008) Excess sludge anaerobic treatment linked together with production of suspension fertilizers. IWA MEMORIAS IX Taller y Simposio Latinoamericano de Digestion Anaerobia. Isla de Pascua, Chile. 19-23 Octubre 2008, 396-400

Uibu M., Kuusik R. (2007) Concept for CO_2 mineralization by oil-shale waste ash in Estonian power production.In: The 3-rd International Green Energy Conference. June 17-21 2007, Västeras, Sweden: 2007. P. 1075-1085.

Uibu, M., Uus, M., Kuusik, R. CO_2 mineral sequestration by oil shale wastes from Estonian power production. *Journal of Environmental Management*. 2009. Vol. 90. P. 1253-1260.

Uibu, M., Velts, O., Kuusik, R. Developments in CO_2 mineral carbonation of oil shale ash. *Journal of Hazardous Materials.* 2010. 174 (1-3), 209-214.