This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 691911

Technology Description (TD) for

Biogas Upgrading Technologies

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Technology Description:

NAME OF TECHNOLOGY	Method of sulfur compound removal from gas flows
ASSIGNMENT OF TECHNOLOGY	The filter bed of mineral matter based on phosphogypsum serving as carrier for microorganisms was developed for system of biogas purification. Biogas purification and bio-sulfur production.

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TECHNICAL READINESS LEVEL **TRL 1** - basic principles observed **TRL 2** - technology concept formulated **TRL 3** - experimental proof of concept **TRL 4** - technology validated in lab **TRL 5** - technology validated in relevant environment (industrially relevant environment in case of key enabling technologies) **TRL 6** - technology demonstrated in relevant environment (industrially relevant environment in case of key enabling technologies) **TRL 7** - system prototype demonstration in an operational environment **TRL 8** - system completed and qualified **TRL 9** - actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space)		1 2 3 **4** 5 6 7 8 9
TECHNOLOGY/EQUIPMENT AVAILABILITY		
PATENT RIGHTS		YES, patented in Ukraine
METHOD OF MAKING THE TECHNOLOGY AVAILABLE	*Licence selling*	NO
	Licence granting	NO
POSSIBLE END USERS OF TECHNOLOGY	*Please name end users/ contacts that should be invited to project workshops*	Wastewater treatment plant utilities, urban waste or livestock treatment facilities, SME with biologically degradable waste

Brief description of the biotechnology:

This project focused on the study the possibility of phosphogypsum utilization in the biotechnological processes for hydrogen sulfide removal from biogas.

Millions of tons of phosphogypsum (PG) is stacked worldwide every year and is progressively considered as an asset more than an environmental burden. PG consists mainly of calcium sulfate dehydrate ($CaSO_4 \cdot 2H_2O$) and contains impurities of not decomposed phosphate, phosphates and silicates.

Phosphogypsum can be used as a biochemical modification of mineral additive for system of biogas purification. Biofiltration involves a filter bed of mineral matter serving both as carrier for microorganisms and as nutrient supplier (granulated phosphogypsum). The biogas from anaerobic bioreactor fed to the bottom of the column through the sleeve. Water was used in the water feed to the biofilter. Air was bubbled into the water that comes from irrigation system to biofilter. At the top of the

column was positioned to drain fitting gas that was clean, and sampling for analysis [Patent of Ukraine for utility model 103687 ***Method of sulfur compound removal from gas flows*****.** Published on 25.12.2015, bul. № 24].

The granulated phosphogypsum (PG) as carrier for microorganisms and as nutrient supplier has the following advantages: it has low cost; it stimulates the development of needful ecological trophic groups of microorganisms; it creates favorable conditions for the formation of biofilm on their surface; the contact surface extends with a gas stream; it is resistant to higher acidity; it has the protection function blocking toxic components; it increases the yield of biosulfur. The natural sorption mechanism is characteristic of bacteria living cells. This mechanism provides important minerals (microelements and macronutrients) for microorganisms in appropriate concentrations, which come from mineral substrate that was PG granules. Cells with specialized transport systems that use energy of ATP hydrolysis provide transport of ions into the cell or selection in the extracellular space. Inside cells metals released in ions or in the form associated with various components of the cytoplasm.

The acidophil association of microorganisms was formed during the desulfurization. This association is able to oxidize hydrogen sulfide to form elemental sulfur (biosulfur) in acid medium.

The advantage of immobilizing bacteria adsorption method on a support of PG is that it allows the binding of bacteria in the mass of the support medium. This creates a stable biomineral structure with effective sulfide conversion to elemental sulfur. The regeneration of granular loading was during its washing with running water and dosed adding of new granules.

The schematic process of biogas purification in bio-sulfurization system is shown in Figure 1.

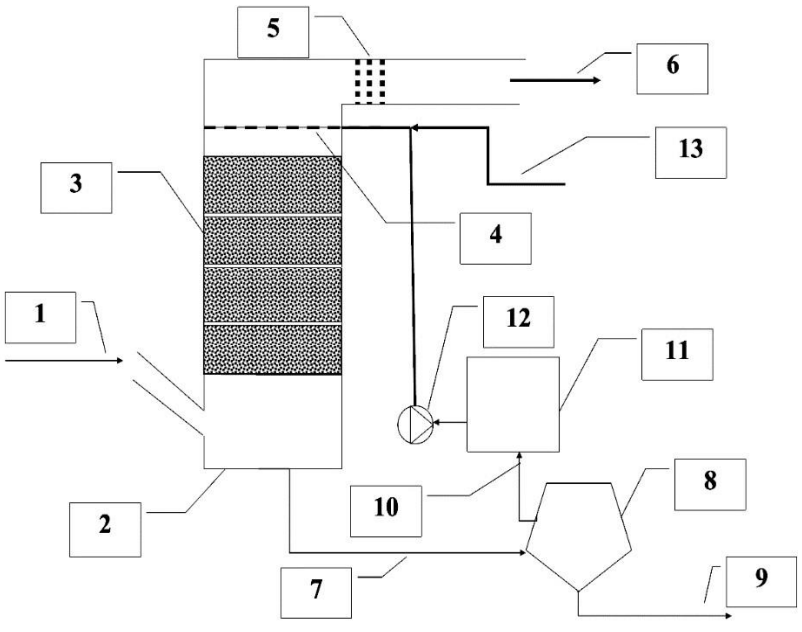

Fig. 1: Biotechnology of gas purification: 1 – gas inflow; 2 – biofilter; 3 – granulated phosphogypsum loading; 4 – irrigation system; 5 – liquid trap; 6 – purified gas; 7 – liquid fraction; 8 – settling tank; 9 – elementary sulfur; 10 – pipeline; 11 – node; 12 – pump; 13 – technical water

The technological scheme works as follows. Gas inflow (1) for purification is transported to the biofilter (2) containing immobilized biomass of Thiobacillus sp. in surface of granulated phosphogypsum loading (3), where hydrogen sulfide is transformed to elemental sulfur form. The flow of gas passed through the liquid trap (5) and freed from the excess moisture. Purified gas (6) is removed from the system. Sulfur flotation occurs in a settling tank (8) and elementary sulfur (9) removed from the system.

The liquid fraction (7) in pipeline (10) is transferred to the node (11), where it is purified to a level suitable for reuse. Then the liquid fraction (7) is transferred to the pump (12) to system of irrigation (4) with technical water (13).

The degree of removal of hydrogen sulfide from biogas increased and reached maximum (99,3%) at pH=5 and 1,5 h. of EBRT.

Immobilization of *Thiobacillus sp*. on granular phosphogypsum

PG granules were suggested to implement the method of adsorptive immobilization of microorganisms. The humidity of granulated support medium of biofilter was increased, which at the beginning of the experiment was in the process of desulfurization unit. The humidity was 10% at the beginning of the experiment, at 30 days was 15% and at 50 day was 17%. This indicates the saturation of its moisture, not only from irrigation systems, but also moisture contained in the sludge formed during sludge digestion biogas. The water film was formed on the surface granulated support medium of PG. There absorbed hydrogen sulfide and ammonia with subsequent transformation of the association of aerobic microorganisms that due process autoselection changed its species composition (the table. 1).

Table 1 Microorganisms immobilized on granulated support medium of the phosphogypsum in the biofilter of desulfurization unit

The duration of experiments	CFU / g (granules)	
	Sulfideoxidizing bacteria	Nitrifying bacteria
10	10_6	10^5
20	10^7	10^4
30	10^8	10^3
40	10^9	10^2

50	10^{10}	10^{2}

In the figure 2 we can see the clusters bacteria of *Thiobacillus sp.* (including by *T. thiooxidans* and *T. ferrooxidans*) immobilized on the surface of the support medium (phosphogypsum) and biosulfur deposits. The total immobilized biomass at the end of batches was of $1{,}9–3{,}7 \cdot 10^{10}$ CFU/g of PG. During period operated desulfurization system this material didn't require regeneration.

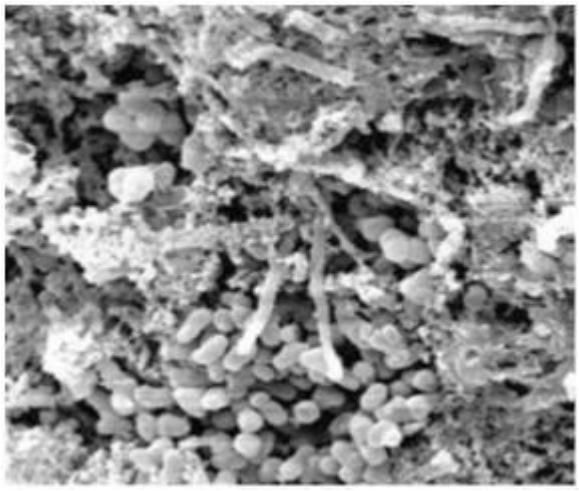

Fig. 2. Scanning electron micrographs of the structure of phosphogypsum granules with Thiobacillus biomass during immobilization process. Magnification: 10 µm

It should be noted that the bacterial matrix penetrated through the fine pores (compared with the size of cells) deep into granules, the cells were subjected to enzyme transformation of mineral components. Thus sulfur was detected on the surface of the granules and subjected to removal. Thus, biosulfur was obtained. This elemental sulfur some different in composition and properties from gaseous sulfur produced using the Claus reaction. Biosulfur contains contaminants in the form of dead biomass of microorganisms and phosphogypsum particles. This sulfur can be used in agriculture.

List of the main published articles using this biotechnology by research group of wastes bio-recycling on the department of applied ecology:

Ye. Chernysh, L. D. Plyatsuk V. Dorda: ***Ecotechnology for hydrogen sulfide removal and production of elemental sulfur***, International Journal of Energy for a Clean Environment, No 15 (2–4), pp. 189–202, 2014 (in English).

Ye. Chernysh, L. D. Plyatsuk: ***Development of biotechnology of hydrogen sulfide removal from biogas using immobilization material based on phosphogypsum*****,** Eastern-European Journal of Eenterprise Technologies, No /6 (74), pp. 49-51, 2015 (in Ukrainian).

Ye. Chernysh, L. D. Plyatsuk: ***Adsorption immobilization of sulfide-oxidizing bacteria in the mass of the support medium made of phosphogypsum*****,** Technology audit and production reserves, No ¾ (23), pp. 4-7, 2015. (in Russian).

L. D. Plyatsuk, Ye. Chernysh: ***Formalization of non-linear patterns of evolutionary ecosystem processes under anthropogenesis influence***, Eastern-European Journal of Eenterprise Technologies, no 2/4, C. 25–31, 2016 (in Russian).

Y. Chernish (Y. Chernysh), L. D. Plyatsuk: ***Opportunity of biochemical process for phosphogypsum utilization***, Journal of Solid Waste Technology and Management, vol.42, no 2, pp.108-115, 2016 (in English).

L. Plyatsuk, Y. Chernysh: ***The Removal of Hydrogen Sulfide in the Biodesulfurization System Using Granulated Phosphogypsum***, Eurasian Chemico-Technological Journal, vol. 18, no 1, pp. 47-54, 2016 (in English).

Y. Chernysh, E. Yakhnenko **: The development of experimental model of gas flows biopurification with granular phosphogypsum using**, Sharing the Results of Research towards Closer Global Cooperation among Scientists: Results of the 7 International Conference: Collection of Research Papers (March 17, 2016) / Responsible editors: M. Prykhodko, S. Tonkykh, A. Mintz – Montreal, Canada: Published by Accent Graphics Communications, pp.68-72, 2016.

Y. Chernysh, E. Yakhnenko, L. Plyatsuk, I. Koziy : ***Study of influence of granulated phosphogypsum load on process of gas cleaning under bio-desulfurization systems***, The scientific heritage, No 8, pp. 109-113, 2017(in Russian).

Patent of Ukraine for utility model 103687
Method of sulfur compound removal from gas flows
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