THE IV BALTIC BIOGAS FORUM

Efficiency of sulphur compounds removal - long-term studies of system applying modified mineral sorbent

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Chemical composition of biogas obtained from different kind raw materials

Component	Unit	Biogas from OFMSW	Biogas from WWTP	Agricultural biogas	Biogas from agricultural and food wastes
Methane	[%]	50 - 60	60 - 75	60 - 75	68
Carbon dioxide	[%]	34 - 38	19 - 33	19 - 33	26
Nitrogen	[%]	0 - 5	0 - 1	0 - 1	-
Oxygen	[%]	0 - 1	<0.5	<0.5	-
Water	[%] (40°C)	6	6	6	6
Hydrogen sulphide	[mg/m^3]	100 - 900	1000 - 4000	3000 - 10000	100
Ammonia	[mg/m^3]	-	-	50 - 100	400
Aromatic compounds	[mg/m^3]	0 - 200	-	-	-
Chlor or fluor organic compounds	[mg/m^3]	100 - 800	-	-	-

Popular sulphur compounds in biogas

Hydrogen sulphide - H_2S

Sulphides - R_2S

Disulphides - RSSR

Dimethyl sulphide - CH_3SCH_3

Methane thiol - CH_3SH

Dimethyl disulphid - CH_3SSCH_3

Carbon disulphide - CS_2

Methyltiophene – C_5H_7S

Ethyltiophene – C_6H_9S

Alkyl disulphides $C_3 – C_{10}$: $C_3H_8S_2 – C_{10}H_{22}S_2$

Alkyltrisulphide C_6 - $C_6H_{14}S_3$

Carbon oxysulphide - COS

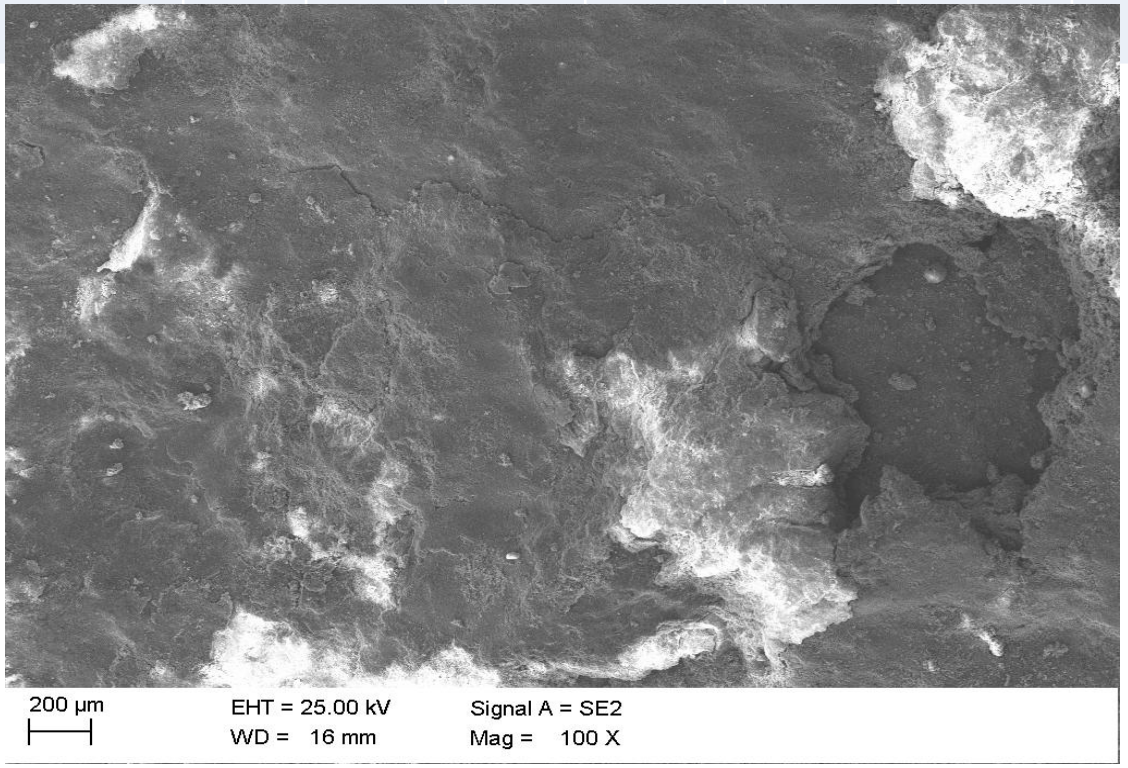
Compound	Abbreviation	Molecular weight [g/mol] at 25°C	Water sollubility [mg/dm^3]	Vapor Pressure at 25°C [kPa]
Trimethyl silanol	-	90	35000	2,13
Hexamethyldisiloxane	L_2	162	0,93	4,12
Octamethyltrisiloxane	L_3	236	0,035	0,52
Decamethyltetrasiloxane	L_4	310	-	0,07
Dodecamethylpentasiloxane	L_5	384	$3,1x10^{-4}$	0,009
Hexamethylcyclotrisiloxane	D_3	222	1,56	1,14
Octamethylcyclotetrasiloxane	D_4	297	0,056	0,13
Decamethylcyclopentasiloxane	D_5	371	0,017	0,02
Dodecamethylcyclohexasiloxane	D_6	445	0,005	0,003


Damaged noise suppressor through sour gasses

View of carbon deposits on cylinders of the engine burning raw biogas after c 1500 working hours.

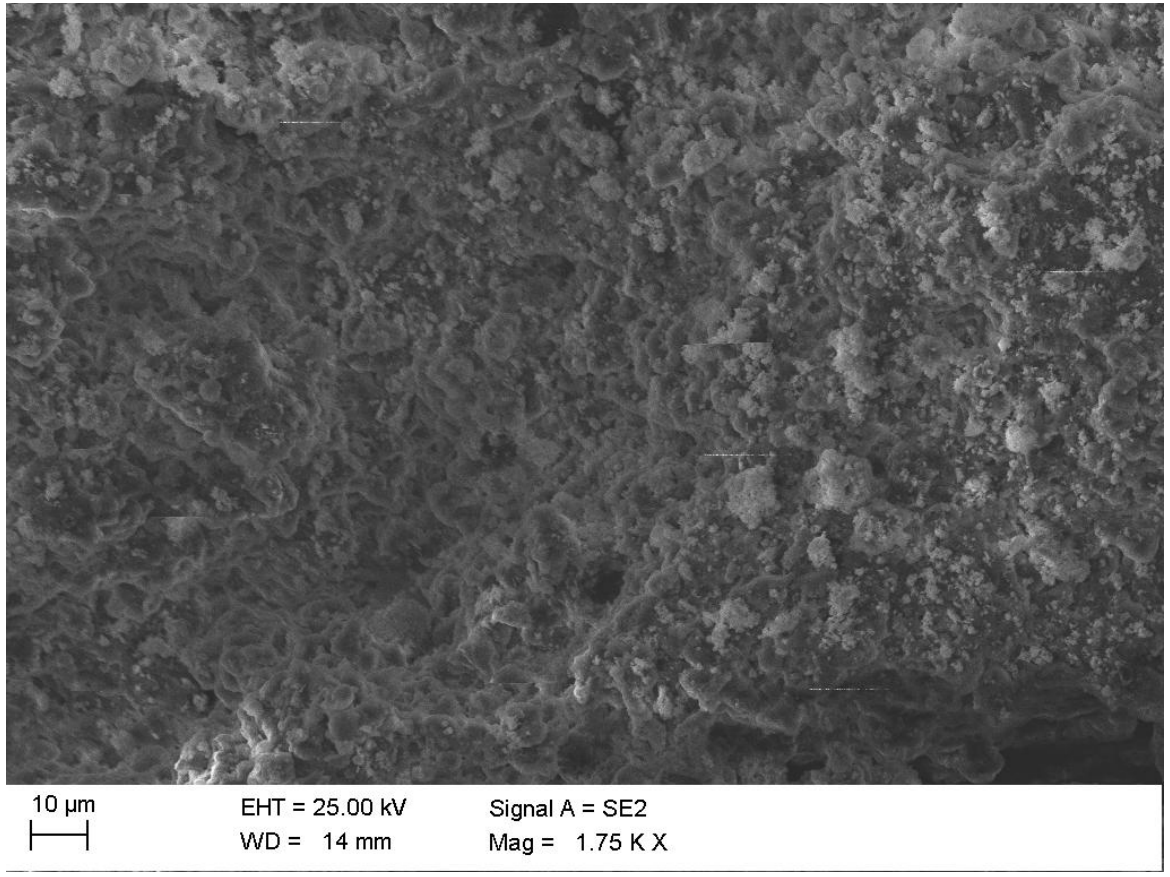
Results of chemical analyses of the carbon deposit produced in the engine using raw biogas

Elements	Ca	S	Zn	Fe	Na	Si	P	Cu	Al	Mn	Mg
Content [%]	22.2	18.6	10.3	1.6	2.6	3.6	3.1	1.5	1.6	0.6	0.6



Microscopic view SEM of the carbon deposit collected from the head of the engine

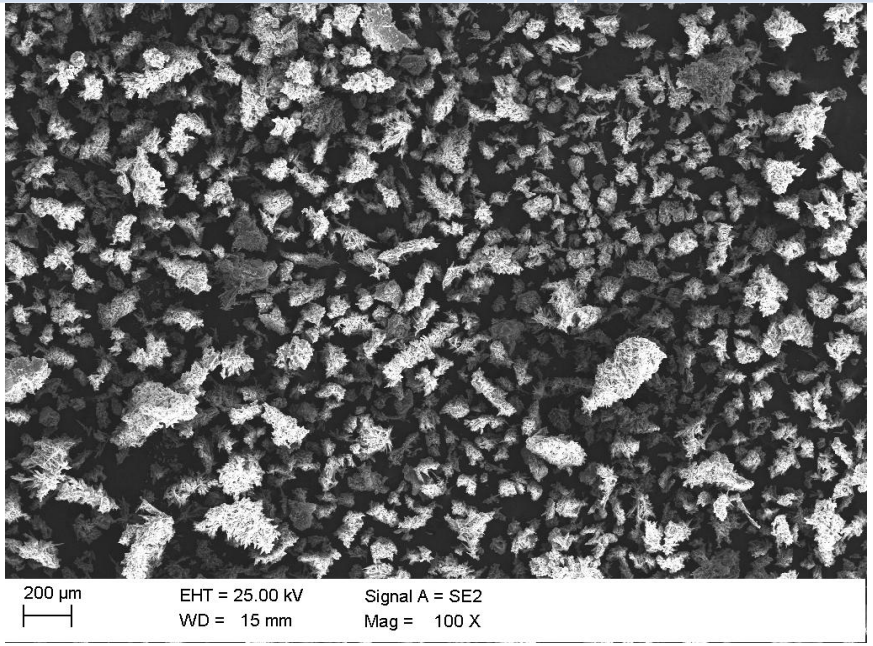
Elements	C	Al	S	Ca	Fe	Na	Zn	P	Si	Ni	Cr
[%]	74.5	3.7	2.2	1.1	0.5	0.4	0.6	0.7	0.2	0.1	0.1



Structure tarry deposit produced on the surface of the heat exchanger

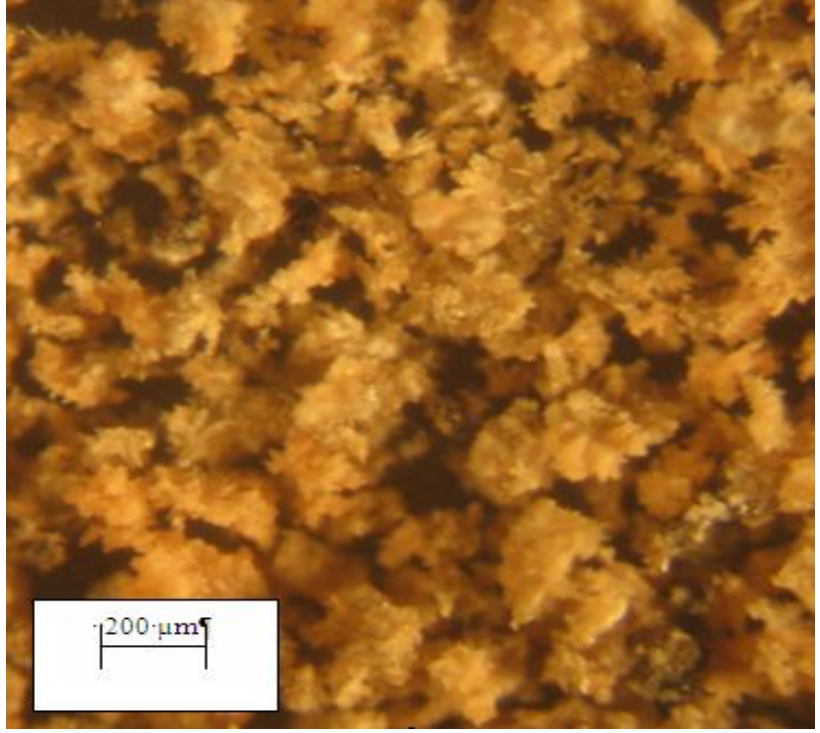
Results of chemical analyses of deposit accumulated in the filter

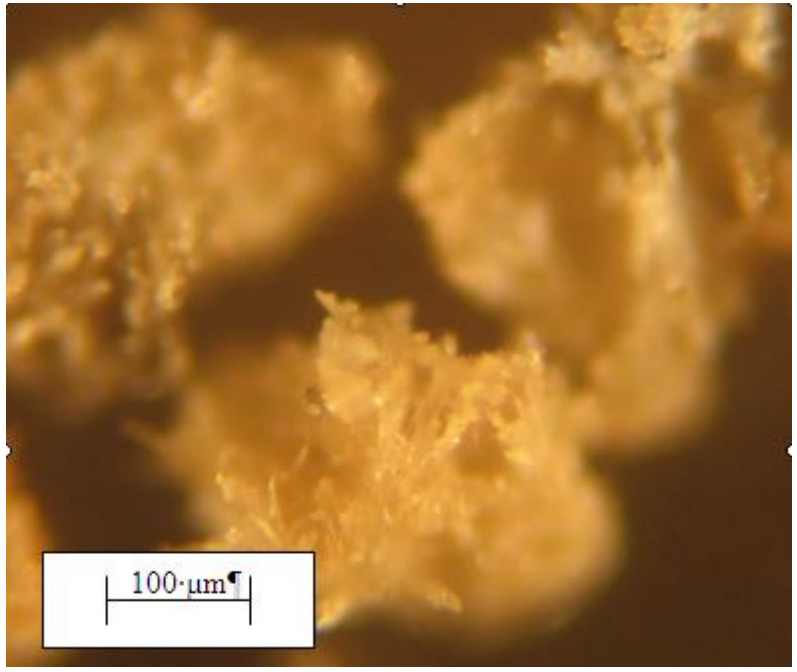
Element	Measurement 1	Measurement 2	Measurement 3	Average
O	40,10	39,58	40,71	40,13
Na	24,45	24,32	25,94	24,90
S	27,85	28,26	23,44	26,52
Ca	0,88	1,04	1,78	1,23
Fe	6,71	6,80	8,13	7,21



Structure of deposit stored up on the filter

View of deposit in the microscope SEM





View of deposit in the optical microscope

Lp.	Name compound	Designation	Value	Unit
1	Chlorine	Cl	< 100	mg/10 kWh
2	Fluorine	F	< 50	mg/10 kWh
3	Total content of chlorine and fluorine	Sum Cl + F	< 100	mg/10 kWh
4	Dust 3 – 10 µm		< 10	mg/10 kWh
5	Oil		<250	mg/10 kWh
6	Silicon	Si	<20	mg/10 kWh
7	Sulphur	S	< 2200	mg/10 kWh
8	Hydrogen sulphide	H_2S	< 1500	mg/10 kWh
9	Ammonia	NH_3	<30	mg/10 kWh
10	Nominal pressure		10	kPa
11	Max. fluctuation of gas pressure		< 0,1	kPa
12	Max. gas temperature		35	°C
13	Max. humidity		80	%

The requirements in relation to the acceptable content of pollutants in biogas

Acceptable content of siloxanes

Internal combustion engines: 5 – 28 mg/m^3

Gas turbines : < 0,1 mg/m^3

Acceptable content of ammonia NH_3

Internal combustion engines: 20 – 50 mg/Nm^3

Acceptable content of H_2S

Energy boilers : do 1000 ppm

Internal combustion engines: 50 – 100 ppm

Gas net: 4 – 7 ppm

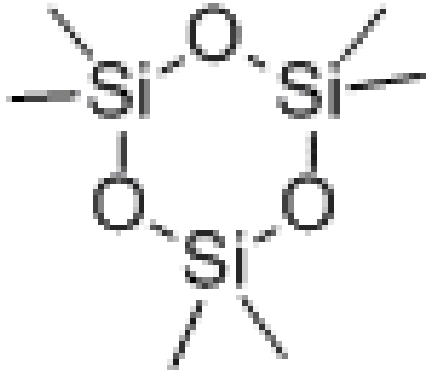
Fuel cells: < 1 ppm

Acceptable content of vapour Hg

Gas net: 30,0$\mu g/m^3$

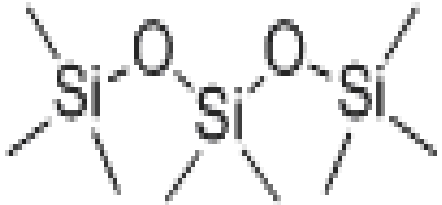
Hexamethyldisiloxane

$C_6H_{18}OSi_2$



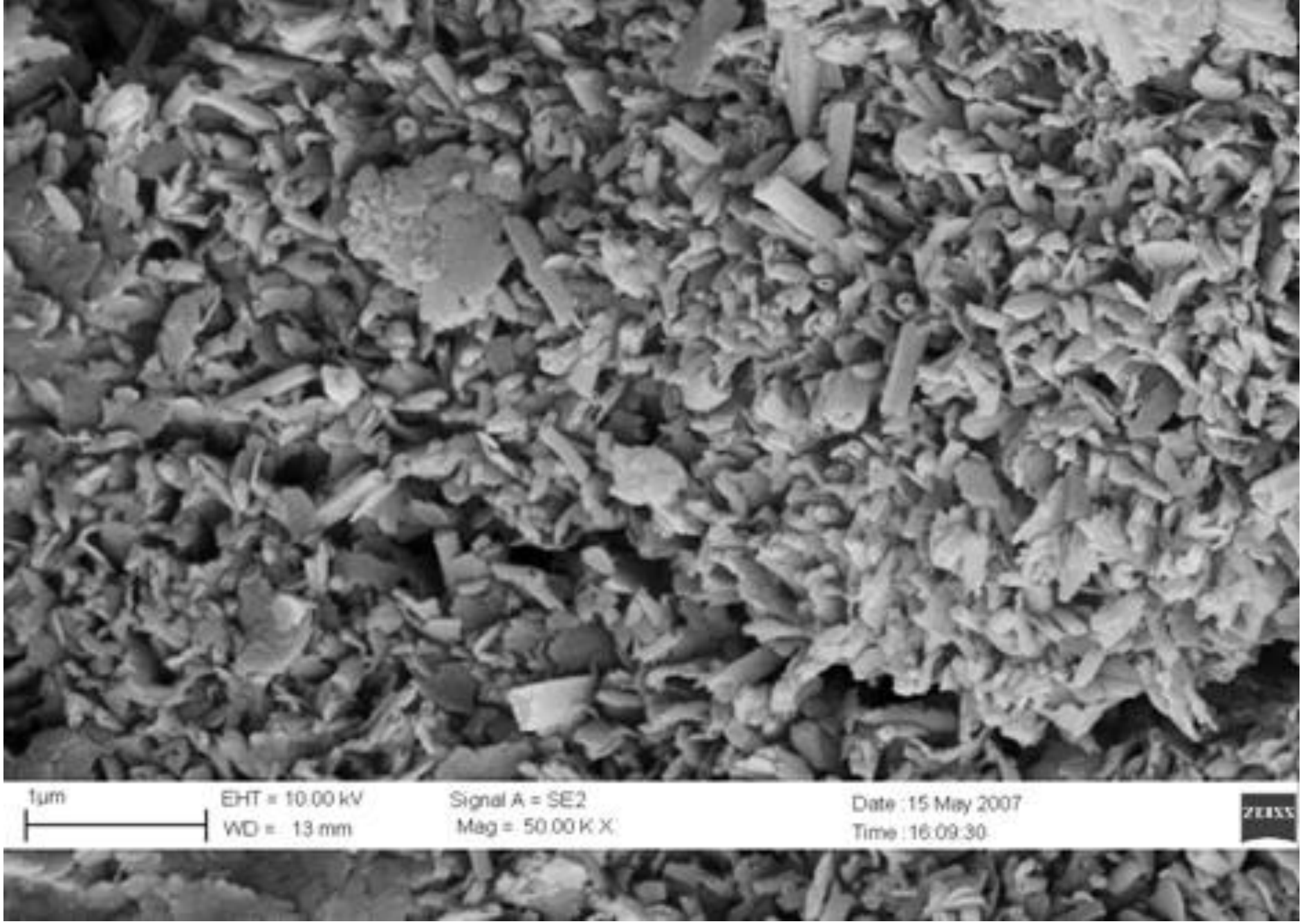
Hexamethylcyclotrisiloxane

$C_6H_{18}O_3Si_3$

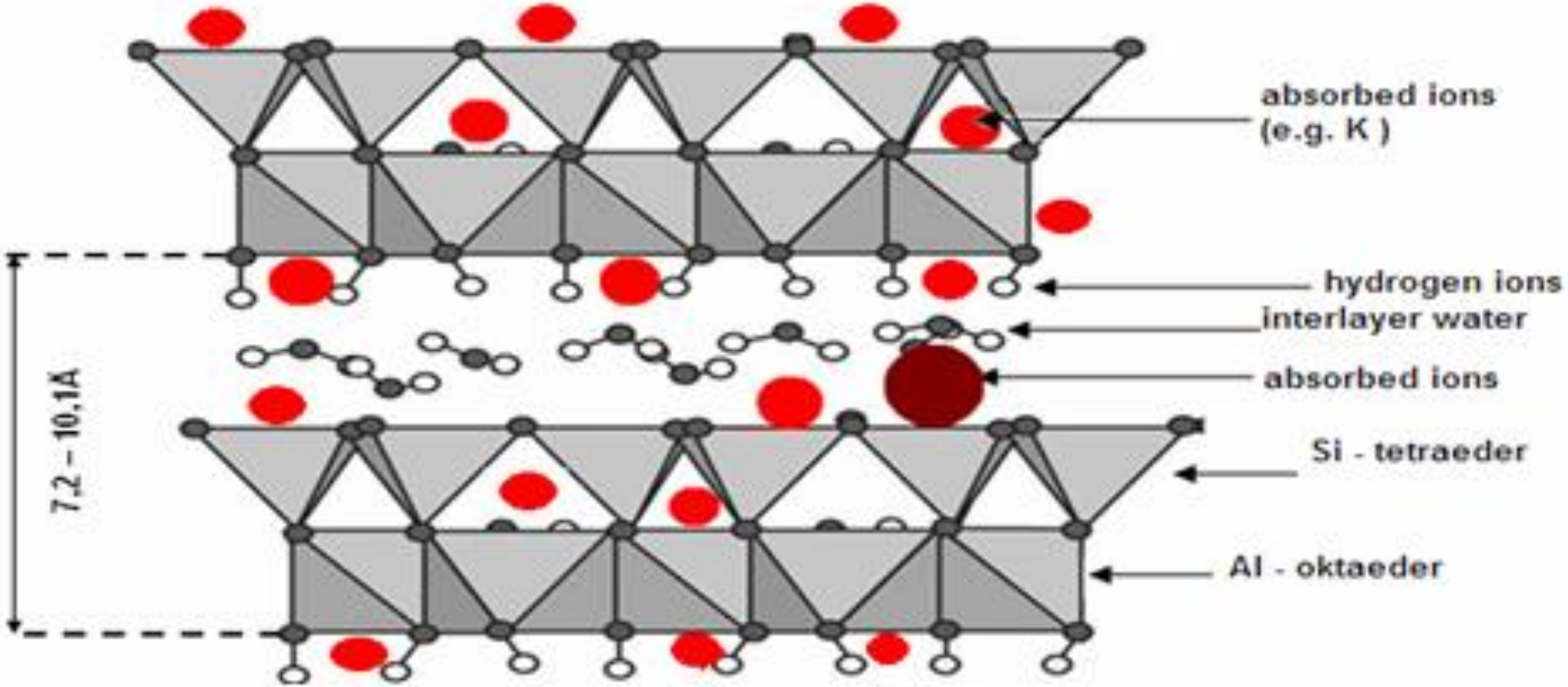


Octamethyltrisiloxane

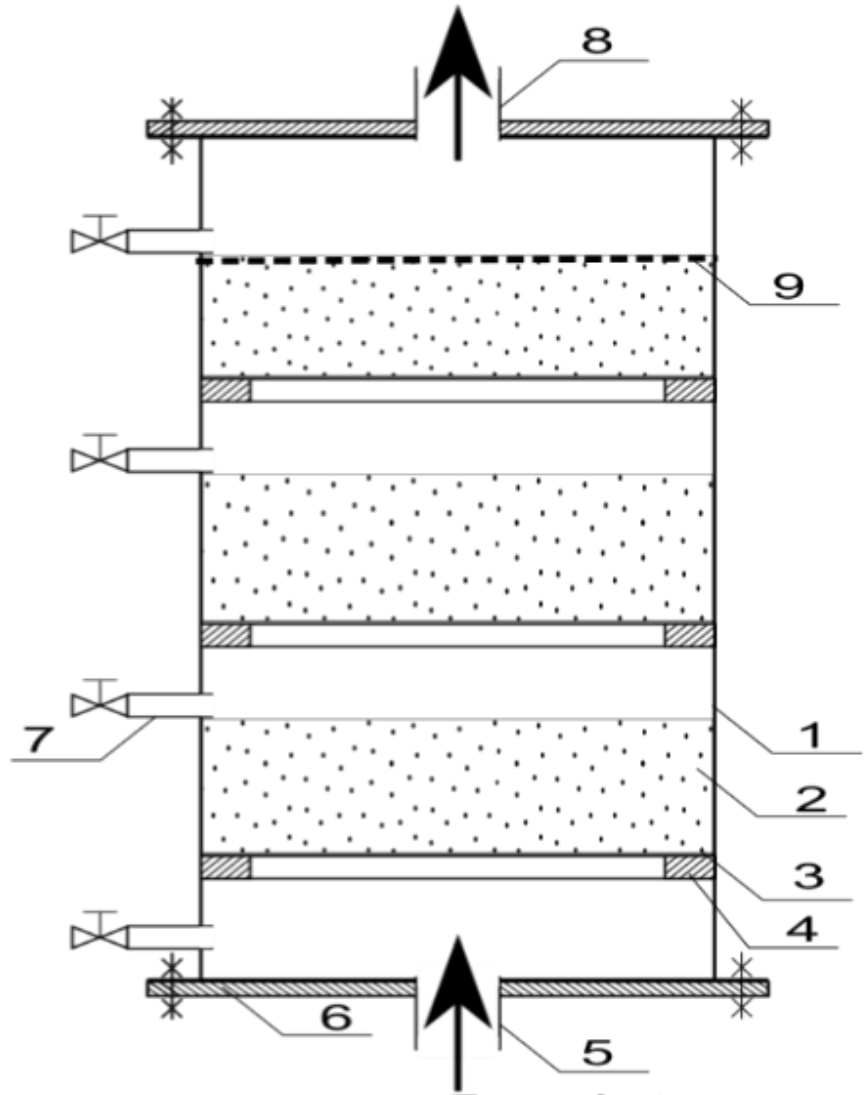
$C_8H_{24}O_2Si_3$



Microscopic view of natural halloisite from the mine Dunino (scale 1 µm)



Layer-cellular structure of halloysite



1 - korpus
2 - sorbent
3 - sito
4 - półka
5 - wlot
6 - pokrywa
7 - króciec probierczy
8 - wylot
9 - włóknina fitracyjna

Change of content of the hydrogen sulphide and ammonia after passing biogas by individual layers of the filter

Measurement	Intake	After I shelf	After II shelf	After III shelf	After IV shelf
H_2S [ppm]	1865	1320	190	20	15
NH_3 [ppm]	2050	1630	1350	960	650
O_2 [%]	0,0	0,0	0,0	0,0	0,0

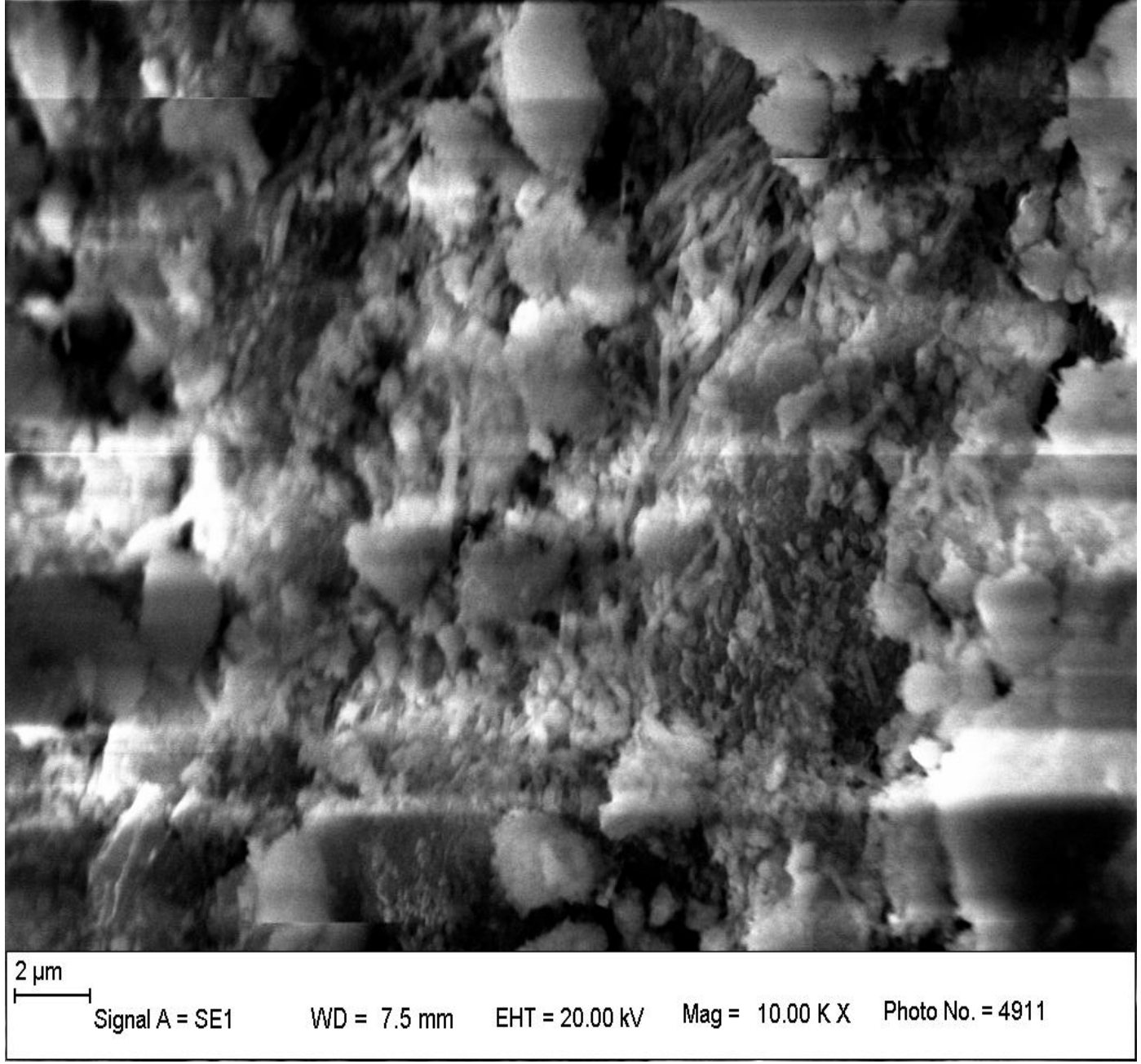
Measurement	Intake	After I shelf	After IV shelf
H_2S [ppm]	1955	245	10
NH_3 [ppm]	1990	1250	425
O_2 [%]	0,0	1,6	1,6

Influence of air addition to the filter

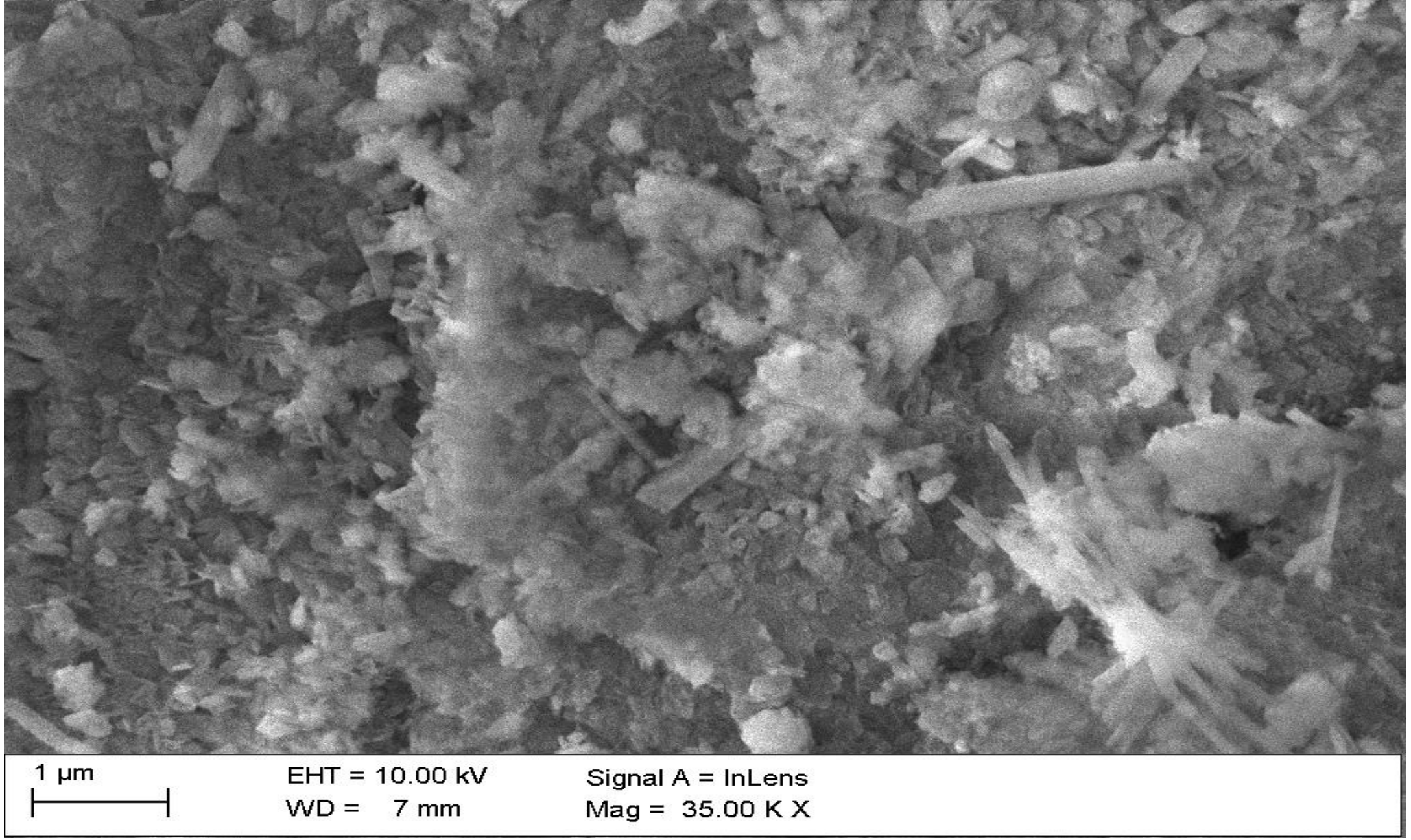
Changes concentration of the hydrogen sulphide after closing the inflow of air

Time after closing the inflow of air [min]	Concentration of H_2S [ppm]
0	385
1	600
2	970
3	1215
4	1310
5	1380
10	1360
20	1370

View of sorbent on the IV shelf (outflow). Privileged places of the flow are visible (darker).



View of sorbent partly saturated



Fresh sorbent

Different kind of filtrs used for biogas purification

New generation filters

New ports in filters

New ports for sampling

New equipment


New
measurements


New filter construction

Filter in Rybnik compost plant

Filter in Chorzów

Compact filter

New compact biogas plant in Proboszczowice


THANK YOU FOR YOUR ATTENTION