



SwissBiogas.com

Additives for Desulphurisation in Anaerobic Digestion

Autark Investments and Projects AG
Dept. SwissBiogas.com
Baarerstrasse 75, CH-6300 Zug
Switzerland

www.swissbiogas.com



SwissBiogas.com presents:
SBGx desulphurisation and gas booster additive



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Desulphurisation, why?

- Protects the CHP unit
- Protects the engines
- Raises the efficiency of the whole plant
- Lowers the operating costs
- Increases the operational safety



Current desulphurisation methods:

- No reactor intervention
- Air injection
- Addition of
 - Ferric chloride, FeCl_3
 - Iron oxide-hydroxide, $\text{FeO}(\text{OH})$
 - Iron oxide, Fe_xO_y



Air injection, why not:

- Impairs fermentation and methane generation (Hinge 2014)
- Atmospheric nitrogen is unnecessarily added to the biogas (Ammonia)
- Excessive introduction of oxygen leads to formation of corrosive sulphurous acid
- % O₂ higher than 0.9% before CHP has a negative effect on efficiency of CHP
- Sulphur deposits formed in the fermenter gas compartment break off from time to time and drop into the substrate
- Risk of explosion
- Increased corrosion: $S + O_2 + H_2O \rightarrow H_2SO_4$
- The air flow should be controlled and adapted regularly:
 - a) Less gas production but same air injection results in too much O₂ and dilution
 - b) Higher gas production with same air injection results in too less O₂ with weak desulphurisation effect



Ferric chloride, why not:

- Reduces volume of produced biogas (12% - 32%)
(Dentel 1982, Johnson 2003, Smith 2008, 2009, Dauknys 2011)
- Forms HCl which penetrates the bacterial membrane
- Classified as dangerous substance
- Considered a corrosive substance
- Releases chlorides during desulphurisation → More corrosive than H₂S

CORROSIVE



IRRITANT





Iron oxide-hydroxide, why not:

- **Iron oxide-hydroxide binds metals.**

These materials are known to bind a wide range of other compounds from water, including trace metals, arsenic, selenium, silicate, and organics. Metals such as manganese, cobalt, nickel, and zinc are known to bind to iron oxide hydroxide in simulated seawater solutions. It has also been claimed that the binding of copper and zinc by natural iron oxide-hydroxide sediments exerts a powerful control on the concentration of copper and zinc in polluted rivers and estuaries. Although not studied in seawater, it has also been observed that phosphate binding by iron oxide-hydroxide actually increases its binding of copper, cadmium, and nickel in freshwater.

- Reference : <http://www.reefkeeping.com/issues/2004-11/rhf/>



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Iron oxide, why yes:

- Eliminates struvite formation
- Lowers H_2S very effectively
- Increases methane production
- Prevents corrosion of plant and CHP
- Reduces HRT



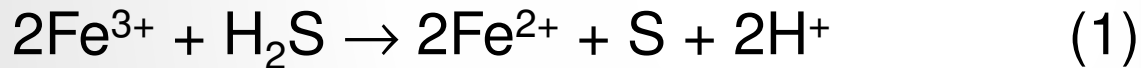
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What happens (inside the reactor):





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Comparison of desulphurisation methods, SBGx by SwissBiogas.com against others:

	<i>SBGx</i>	<i>Iron oxide</i>	<i>Iron oxide-hydroxide</i>	<i>Iron chloride</i>	<i>Air injection</i>
<i>Investment into</i>					
Storage and Handling	low	low	low	high	none
Dosing Equipment	none / low	none / low	medium	medium	medium
<i>Risk of / to</i>					
Exposure / Personnel	low	low	low	high	none
Explosion	low	low	low	low	high
Corrosion	low	low	low	high, HCl	high, H ₂ SO ₄
Incompatibility	low	low	low	high	high
Gas Impurities	low	low	low	low	high
Reaction Products	none	none		HCl	H ₂ SO ₄
<i>Characteristics</i>					
Reactive Content	> 60%	30% - 60%	10% - 15%	10% - 14%	none
Digestion Speed / Volume	high	low	low	high	low
Deposit Effect	high	high	medium	none	none
Methanogen Growth	increased	normal	normal	negative	negative
Gas Yield over Normal	higher	normal	normal	negative	negative
Trace Element Addition	not necessary	required	required	required	required
Shelf Life	> 12 months	> 12 months	< 12 months	< 12 months	none
Price per chem. Reaction	medium	high	medium	high	none



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The components of SBGx as base
before individual adjustments to
customers' requirements

Note: The industry-leading high
content of reactive Fe_xO_y

SBGx	[%]
FeO + Fe ₂ O ₃	> 70
MnO	< 1.0
C	< 0.5
Cr ₂ O ₃	< 0.5
CaO	< 0.5
K ₂ O	< 0.5
Al ₂ O ₃	< 0.5
SiO ₂	< 0.5
ZnO	< 0.5
Na ₂ O	< 0.2
CuO	< 0.2
S	< 0.1
TiO ₂	< 0.1
MgO	< 0.1
NiO	< 0.1
P ₂ O ₅	< 0.1
MoO ₃	< 0.05
V ₂ O ₅	< 0.01
BaO	< 0.01
CoO	< 0.01
PbO	< 0.01
CdO	< 0.01
SnO ₂	< 0.01
WO ₃	< 0.01
Cl	< 0.01
SeO ₂	< 0.01

Sample application of SBGx in practice

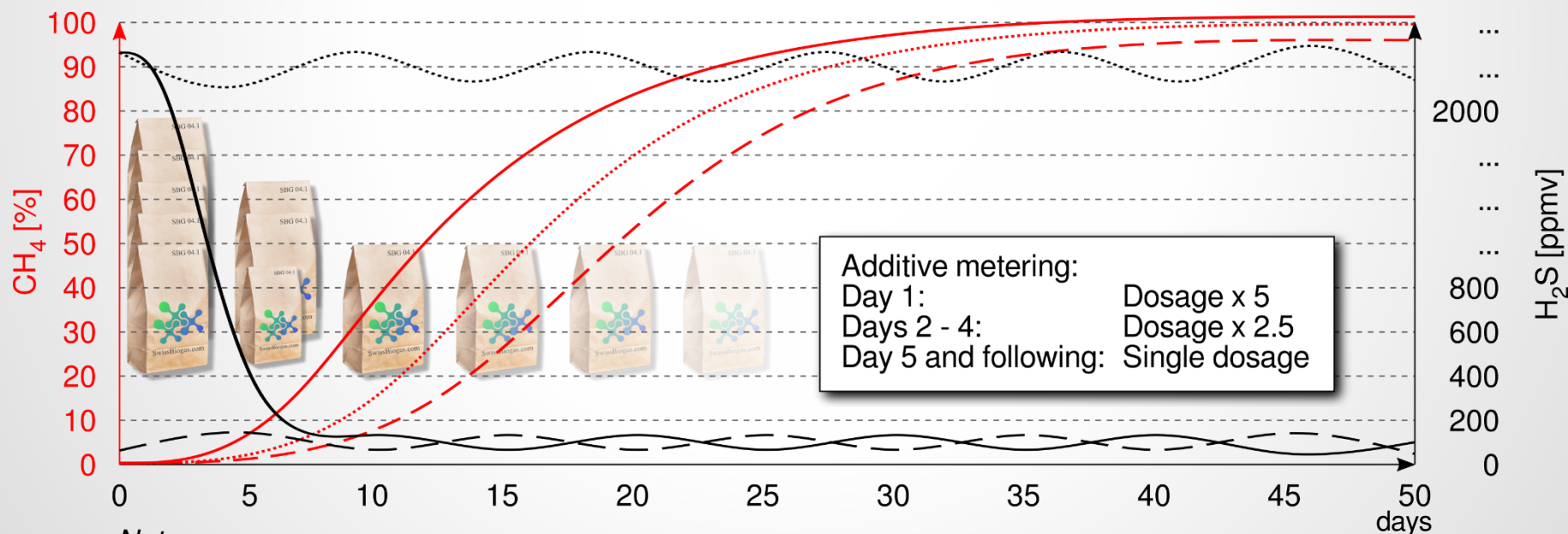
Comparison of CH_4 and H_2S developments

Legend

- SBGx treated, solid
- Untreated, dotted
- FeCl_3 treated, dashed

CH_4

H_2S





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How we pack and ship:

Delivered in powder form, in

- 20 kg bags, or as per
- individual requirements

Please contact your agent for availability.



2017 Test results by specific waste category: *Kitchen Waste*

- Additive: EG 1117 (old naming convention)
- Duration: 51 days

Increase of methane production overall:

- Average: 13.5%
- High: 19.3%

Increase rate of methane production per unit VS:

- Average: 16.3%
- High: 23.2%

Speeding up of fermentation rate; Peak of daily methane production:

- Average w/o additive: Day 13, 183.1 ml/day
- Average w/ additive: Day 10, 200.5 ml/day
- High: Day 10, 206.7 ml/day

Remark: All results above achieved within 43 days!

Orig. report (2018, Q1) available upon request



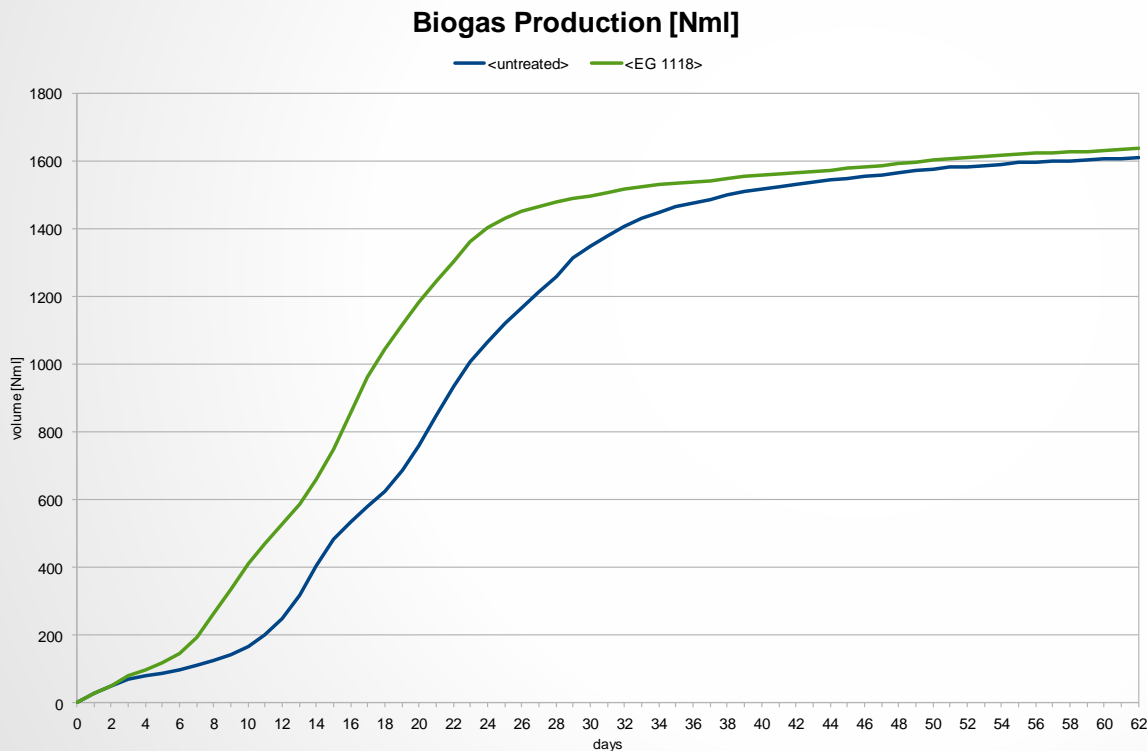
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2018 Effectivity test by specific waste category: *Corn Straw*



Slide 1 of 2

The maximum duration of the test periods was 79 days. As some tests were terminated between day 62 and 79, only the first 62 days are analysed.

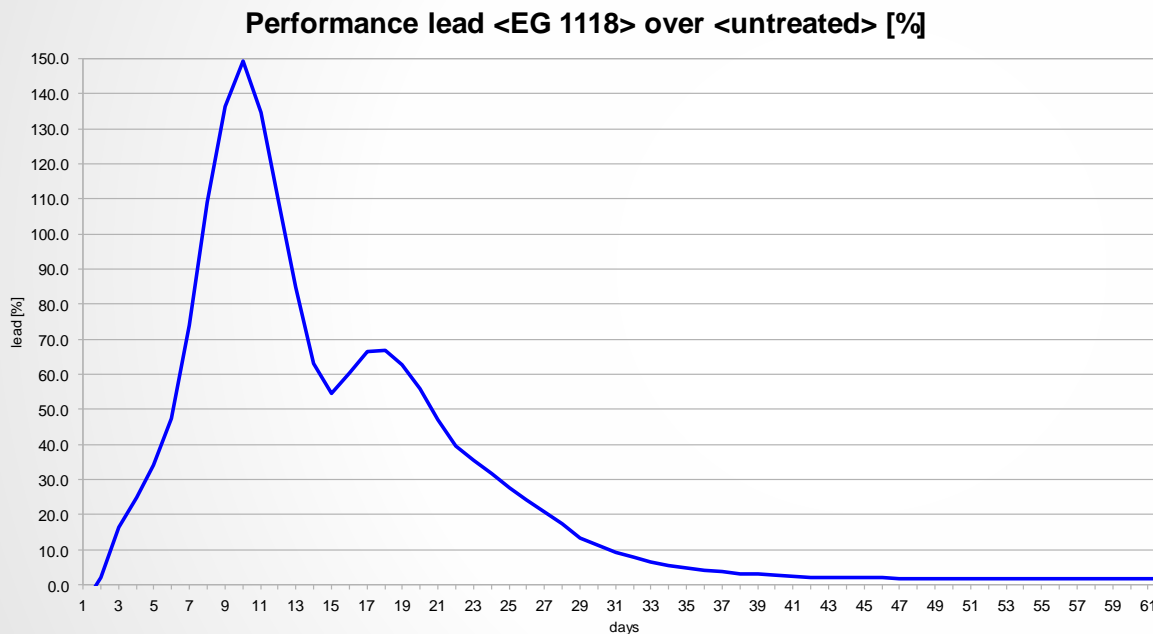
During the first 30 days, the tests showed an increased effectivity in biogas production of the substrate treated with the SBG additive EG 1118 (green, old naming convention).

Several tests were performed and the graphs show the average (“<...>”) biogas production.

Total produced biogas with the untreated substrate after 62 days: 1609.7 Nm



2018 Effectivity test by specific waste category: *Corn Straw*



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The graph shows the advantage [%] of the additive treated substrate over the untreated substrate.

If the total produced biogas with the untreated substrate after 62 days (1609.7 Nml) is defined as 100%, 90% was reached after:

- 34 days with the untreated substrate (1448.0 Nml)
- 26 days with the EG 1118 additive treated substrate (1449.6 Nml); Performance lead: 24.3%

If a short retention time in a reactor is key, the substrate treated with the EG 1118 additive has a significant advantage during the first 30 days. (see above)

Even at day 30, the EG 1118 additive treated substrate still has a lead of 11.1% in biogas production over the untreated substrate.

- untreated: 1347.1 Nml (83.7% of 1609.7 Nml)
- EG 1118: 1497.2 Nml (93.0% of 1609.7 Nml)



2018 Test at a German biogas plant (EG 1118, old naming convent.)

Duration	Input					Output				
	Liq. Pig Man. [kg]	Grain [kg]	Maize [kg]	Recirculate [kg]	Total [kg]	CH ₄ [Vol%]	CO ₂ [Vol%]	O ₂ [Vol%]	H ₂ S [ppm]	Energy [kWh]
5.9-16.9 12 days prior	18'639.00 (40.95%)	551.00 (1.21%)	26'330.00 (57.84%)	77'377.00	122'897.00	51.00	42.00	0.90	108.00	12'307.00
27.10-7.11 last 12 days	14'894.00 (37.14%)	495.00 (1.23%)	24'708.00 (61.62%)	75'854.00	115'951.00	50.00	48.00	1.10	77.00	12'999.00
Change [%]	-20.09	-10.16	-6.16	-1.97	-5.65	-1.96	14.29	22.22	-28.70	5.62

Methane potential calculation, based on "Biogas yield by substrate", page 815
Production from selected plants and by-products:

Substrate	Biogas [m ³ /t]	CH ₄ ratio [%]	CH ₄ [m ³ /t]
Pig Slurry:	500	65	325.0
Grain Decoction:	560	66	369.6
Maize Silage:	580	52	301.6

Source: *THE EFFECT OF SUBSTRATE ON THE AMOUNT AND COMPOSITION OF BIOGAS IN AGRICULTURAL BIOGAS PLANT*
Nr III/2/2015, POLSKA AKADEMIA NAUK, Oddział w Krakowie, s. 809–818
Komisja Technicznej Infrastruktury Wsi
By: Joanna Kazimierowicz, Białystok University of Technology
Link: <http://dx.medra.org/10.14597/infraeco.2015.3.2.065>

Comparison of the reactor's methane potential based on the substrate input:

Duration	Pig Slurry [m ³]	Grain Dec. [m ³]	Maize [m ³]	Recirculate [m ³]	Total CH ₄ [m ³]
5.9-16.9	6'057.68	203.65	7'941.13	24'141.99	38'344.44
27.10-7.11	4'840.55	182.95	7'451.93	23'600.56	36'075.99
Change [%]	-20.09	-10.16	-6.16	-2.24	-5.92

Assumption:

The recirculate has the same mix ratio as the freshly added substrate.

→ If a potential of 38,344.44 m³ of CH₄ result in measured 12,307.00 kWh of energy, then a potential of 36,075.99 m³ of CH₄ should mathematically result in 11,578.92 kWh (-5.92%) of energy, without additives.

Duration	Energy w/o additives [kWh]	Energy w/ additives [kWh]
5.9-16.9	12'307.00	-----
27.10-7.11	calculated: 11'578.92	measured: 12'999.00
Change [%]	-5.92	-----

→

Effect of the SwissBiogas.com additives:

Increase from 11,578.92 kWh to 12,999.00 kWh: 12.26%