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SwissBiogas.com
Additives for Results-Driven Anaerobic Digesters

SwissBiogas.com presents:
SBGx desulphurisation and gas booster additive

v1.37

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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

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Current desulphurisation methods:

- No reactor intervention
- Air injection

  Addition of
  - Ferric chloride, $FeCl_3$
  - Iron oxide-hydroxide, $FeO(OH)$
  - Iron oxide, Fe_xO_y

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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
- % O_2 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 O_2 and dilution
  b) Higher gas production with same air injection results in too less O_2 with weak desulphurisation effect

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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 H_2S

CORROSIVE

IRRITANT

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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):

$2Fe^{3+} + H_2S \rightarrow 2Fe^{2+} + S + 2H^{+}$ (1)

$2Fe^{2+} + (1/2)\ O_2 + H_2O \rightarrow 2Fe^{3+} + 2OH^{-}$ (2)

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

	SBGx	*Iron Oxide*	*Iron Oxide-Hydroxide*	*Iron Chloride*	*Air Injection*
Investment into					
Storage and Handling	outside, low	covered, low	covered, low	covered, high	not applicable
Dosing Equipment	none / low	none / low	medium	medium	high
Risk of / to					
Exposure / Personnel	low	low	low	high	n. a.
Explosion	low	low	low	low	high
Corrosion	low	low	low	high, HCl	high, H_2SO_4
Gas Impurities	low	low	low	low	high
Reaction Products	none	none	none	HCl	H_2SO_4
Other Characteristics					
Chemical Composition	FeO and Fe_2O_3 **	Fe_2O_3	FeO(OH)	$FeCl_2$ or $FeCl_3$	n. a.
Reactive Iron Ion Content	> 60%	30% - 60%	10% - 15%	10% - 14%	n. a.
Reaction Speed	high	low	low	high	low
Deposit / Buffer Effect	high	high	medium	none	none
Effect on Bacterial Health	positive	normal	normal	negative	negative
Effect on Gas Yield	positive	normal	normal	0 to minus 32% ***	negative
Trace Element Addition	not necessary	required	required	required	required
Shelf Life	> 12 months	> 12 months	< 12 months	< 12 months	n. a.
Price per chem. Reaction	medium	high	medium	high	n. a.

v1.07

** See *www.swissbiogas.com/Resources - Download Area/Effects of Different States of Fe on Anaerobic Digestion: A Review*

*** See *www.swissbiogas.com/Resources - Download Area/The effect of iron salt on anaerobic digestion and phosphate release to sludge liquor*

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Calculation of the Reactive Iron Ion Content (RIIC)

The sole differentiating factor of any Fe-based additive is its Reactive Iron Ion Content (RIIC; Higher = Better). RIIC is a unit, introduced and used by SwissBiogas.com, to reliably project the potential of additives to bind sulphur and to support the health of methanogens.

The RIIC of any additive can be calculated as follows:

			Oxidation state
• FeO, Wuestite:	Content of FeO [%]	x 0.7773	Fe^{2+}
• Fe_2O_3, Hematite:	Content of Fe_2O_3 [%]	x 0.6994	Fe^{3+}
• Fe_3O_4, Magnetite:	Content of Fe_3O_4 [%]	x 0.7236	$Fe^{2.67+}$
• $FeCl_2$, Ferrous Chloride:	Content of $FeCl_2$ [%]	x 0.4406	Fe^{2+}
• $FeCl_3$, Ferric Chloride:	Content of $FeCl_3$ [%]	x 0.3443	Fe^{3+}
• FeO(OH), Ferric Oxyhydroxide:	Content of FeO(OH) [%]	x 0.6285	Fe^{3+}
• $Fe(OH)_2$, Ferrous Hydroxide:	Content of $Fe(OH)_2$ [%]	x 0.6215	Fe^{2+}
• $Fe(OH)_3$, Ferric Hydroxide:	Content of $Fe(OH)_3$ [%]	x 0.5226	Fe^{3+}

Examples:

1. SwissBiogas.com SBGx: RIIC > 60%
2. Additive X: FeO(OH) content = 73% → RIIC = 73% x 0.6285 = 45.9%
3. Additive Y: $FeCl_3$ content = 40% → RIIC = 40% x 0.3443 = 13.8%

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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 ions > 60%

SBGx	*[%]*
FeO	> 35
Fe_2O_3	> 35
MnO	< 1.0
CaO	< 0.5
Al_2O_3	< 0.5
MgO	< 0.5
Cr_2O_3	< 0.2
Zn	< 0.1
Cu	< 0.1
NiO	< 0.1
K_2O	< 0.05
CoO	< 0.05

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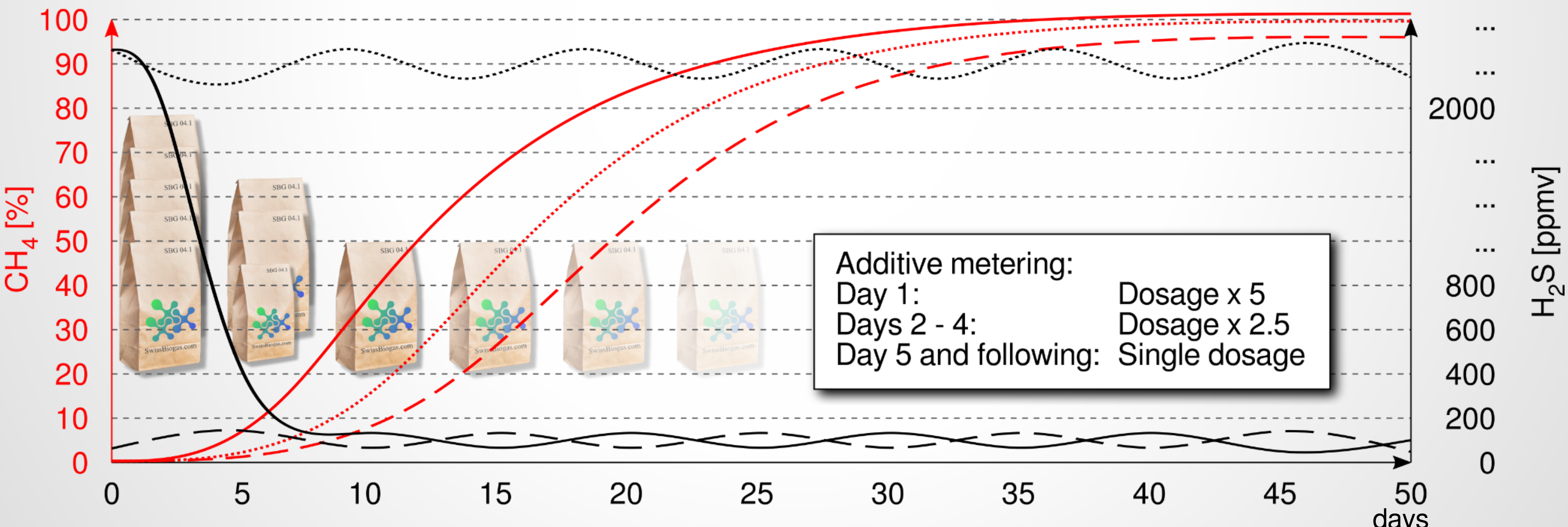
Sample application of SBGx in practice

Comparison of CH_4 and H_2S developments

Legend: CH_4 (red), H_2S (black)
- SBGx treated, solid
- Untreated, dotted
- $FeCl_3$ treated, dashed



Note:
100% CH_4 = Total reclaimed CH_4 by untreated process within 50 days

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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.

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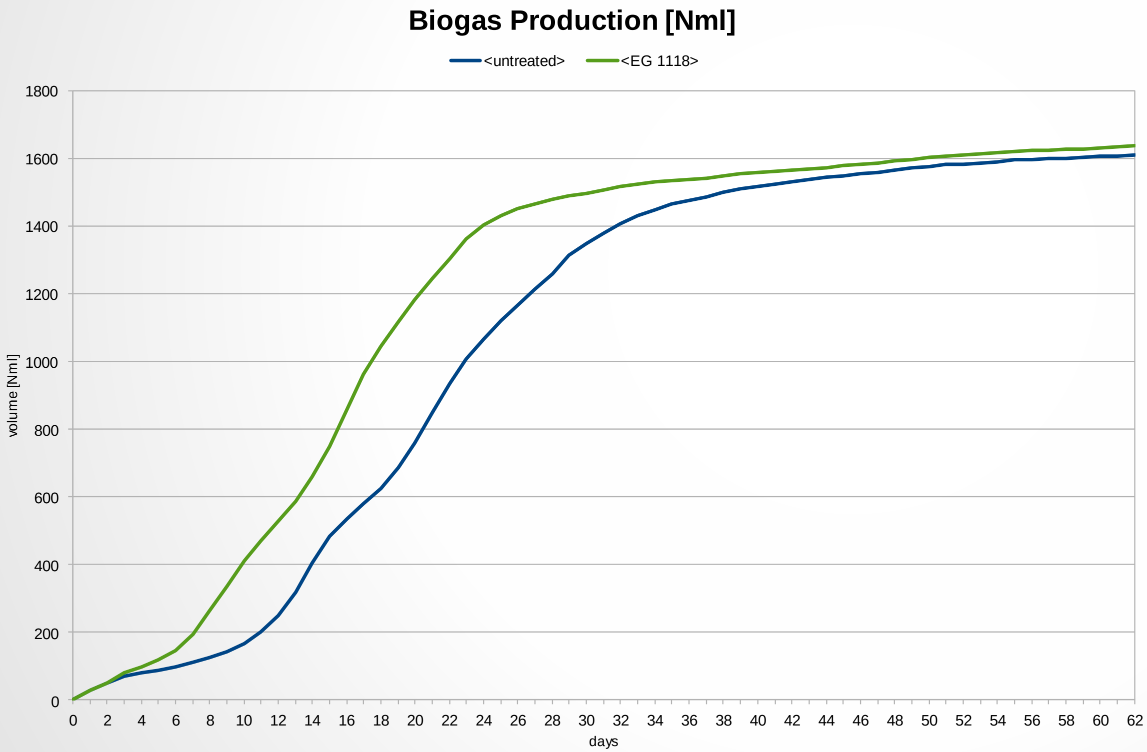
2018 Effectivity test by specific waste category: *Corn Straw*



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 Nml

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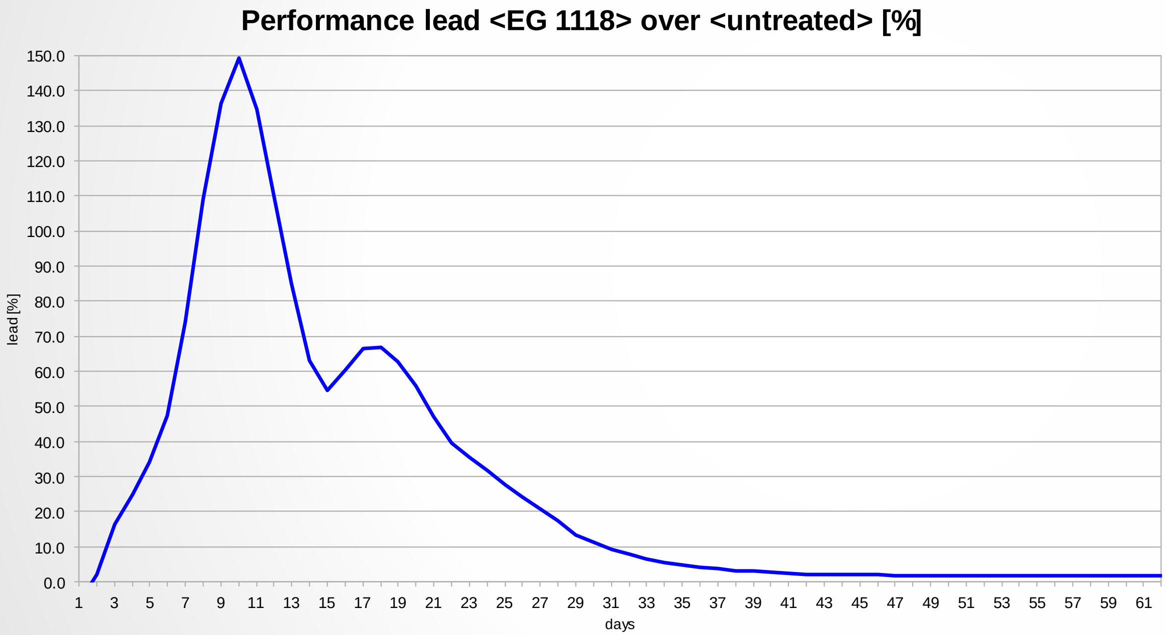
2018 Effectivity test by specific waste category: *Corn Straw*



Slide 2 of 2

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)

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

	Input					Output				
Duration	Liq. Pig Man. [kg]	Grain [kg]	Maize [kg]	Recirculate [kg]	Total [kg]	CH_4 [Vol%]	CO_2 [Vol%]	O_2 [Vol%]	H_2S [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 [m³/t]	CH_4 ratio [%]	CH_4 [m³/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, Bialystok 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 [m³]	Grain Dec. [m³]	Maize [m³]	Recirculate [m³]	Total CH_4 [m³]
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 CH_4 result in measured 12,307.00 kWh of energy, then a potential of 36,075.99 m³ of CH_4 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%